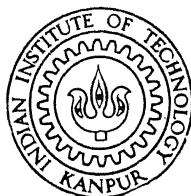# HYDROBORATION STUDIES ON DIENES

BY

INDU MEHROTRA

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

1972

HYDROBORATION STUDIES ON DIENES

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

BY
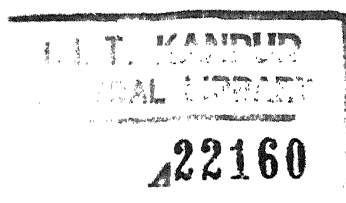INDU MEHROTRA

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
1972

सर्वमङ्गल - माङ्गल्ये,
      शिवे   सर्वार्थसाधिके ॥
शरण्ये त्र्यम्बके गौरि !,
      नारायणि ! नमोऽस्तु ते ॥

STATEMENT

I hereby declare that the research work embodied in this thesis 'Hydroboration Studies on Dienes' is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology Kanpur, under the supervision of Professor D. Devaprabhakara.

The extent of information derived from the existing literature has been indicated in the body of the thesis at appropriate places, giving the source of information.
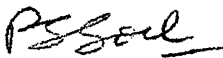
Indu Mehrotra

DEPARTMENT OF CHEMISTRY
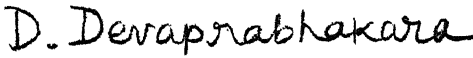INDIAN INSTITUTE OF TECHNOLOGY KANPUR, INDIA

CERTIFICATE I

This is to certify that Miss Indu Mehrotra has satisfactorily completed all the courses required for the Ph.D. degree programme in Chemistry. These courses include:

Chm 501	Advanced Organic Chemistry I
Chm 502	Advanced Organic Chemistry II
Chm 521	Chemical Binding
Chm 523	Chemical Thermodynamics
Chm 524	Modern Physical Methods in Chemistry
Chm 541	Advanced Inorganic Chemistry I
Chm 614	Organic Photochemistry
Chm 615	Electrocyclic Reactions
Chm 624	Valence Bond and Molecular Orbital Theory
Chm 800	General Seminar
Chm 801	Graduate Seminar
Chm 900	Graduate Research

Miss Indu Mehrotra has successfully completed her Qualifying Examination in October, 1968.

(P.S. Goel)
Head,
Chemistry Department

(D. Devaprabhakara)
Convener
Departmental Post-
Graduate Committee

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CERTIFICATE II

Certified that the work contained in this thesis entitled: "HYDROBORATION STUDIES ON DIENES" has been carried out by Miss Indu Mehrotra under my supervision and the same has not been submitted elsewhere for a degree.

D. Devaprabhakara

D. Devaprabhakara
Thesis Supervisor

Kanpur:
April 1972

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ACKNOWLEDGEMENTS

commendable.

Lastly, author sincerely thanks Mr. R.D. Singh for competent typing, Mr. B.N. Shukla and Mr. R.S. Chauhan for cyclostyling the thesis.

PREFACE

The thesis entitled as "Hydroboration Studies on Dienes" is comprised of five chapters. Each chapter has further been subdivided into (1) Abstract, (2) Introduction, (3) Results and Discussion, (4) Experimental and (5) References. Introduction to each chapter covers a brief literature survey relevant to the title of the chapter.

In the first chapter, cyclic hydroboration-oxidation of various medium-ring dienes other than 1,2-dienes has been described. The intermediacy of the bicyclic organoboranes has been proposed, and the synthesis of cis-1,5-cyclic diols has been achieved. The results are consistent through-out the structural variations among the dienes except in two cases. cis,cis-1,3-Cyclodecadiene leads to the formation of trans,cis-β-decalol, possibly not via the bicyclic organoborane as intermediate. The isomerization of the bicyclic organoborane obtained from cis,trans-1,5-cyclodecadiene does not follow the usual customary path leading to the formation of the most stable bicyclic organoborane, instead it goes to vinylic boron compound which undergoes rehydroboration-oxidation to give alcohol and ketone. The diversity in the results is definitely reflected by the conformational variations of the various dienes.

The reactions of the bicyclic organoboranes with silver nitrate in alkaline medium (obtained from medium ring dienes) form the subject matter of the second chapter. The reaction has been

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done with various amounts of silver nitrate (catalytic amount, 1:1 and 3:1 silver nitrate to diene ratio). It has been shown that at least 1:1 molar ratio of silver nitrate to diene is needed to achieve complete reaction of the bicyclic organoborane. Furthermore, the intermediacy of a bororadical and diradical has been postulated with 1:1 and 3:1 silver nitrate to diene ratios respectively in order to explain the formation of ketones and olefins.

The last three chapters deal with the hydroboration of 1,2-dienes (allenes). Third chapter deals with the study on the dihydroboration of cyclic as well as acylic allenes. Dihydroboration followed by hydrogen peroxide oxidation has been shown to give a variety of products ranging from hydrocarbons to diols. The unusual feature of this project is the formation of a mixture of olefins on treating the intermediate diboro compound with chromium trioxide in pyridine. The participation of another boron has been put forward in order to explain these results.

The last two chapters specifically describe some of the reactions of the allylic organoboranes obtained in situ by the monohydroboration of mono- and 1,1-disubstituted allenes with disiamylborane. Fourth chapter comprises essentially the reaction of these allylic organoboranes with acetic acid. The reaction of allylic organoborane obtained from 3-phenyl-1,2-butadiene (DSPBB) with aldehydes and ketone has been summarized in the last chapter of the thesis. Allylic rearrangement has

been observed in all the cases. The treatment of allylic organoborane with acetic acid gives exclusively terminal olefin. β, γ-Unsaturated alcohols have been obtained by reacting DSPBB with aldehydes and ketone. These results have been explained <u>via</u> a six-membered transition state involving allylboron moiety of the organoborane and the hydroxy group of acetic acid or carbonyl group of aldehydes and ketone.

CONTENTS

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CHAPTER I

CYCLIC HYDROBORATION
OF MEDIUM-RING DIENES

I.1 ABSTRACT

The study on the cyclic hydroboration of medium-ring dienes is described. The hydroboration-isomerization-oxidation of cis,cis-1,3-cyclooctadiene, cis,cis-1,3-, cis,cis-1,4-, cis,cis-1,5-cyclononadiene, and cis,cis-1,6-cyclodecadiene proceeds preferentially to the cis-1,5-cyclic diols. These results can be explained via the bicyclic organoboranes. Thus, the procedure described provides a convenient stereospecific synthesis of cis-1,5-cyclic diols in nine- and ten-membered rings for the first time. Our results with cis,cis-1,3-, cis,cis-1,4- and cis,trans-1,5-cyclodecadiene reveal the configurational and conformational effects in cyclic hydroboration. Furthermore, these reactions appear to be interesting from mechanistic point of view.

I.2 INTRODUCTION

Recent developments in the field of organoboranes have now revealed a vast amount of their chemistry and their promise to become reagents of choice for many transformations in organic synthesis. The earlier work of Brown and coworkers[1-6] was directed towards finding out suitable reagents which would provide a convenient and more practical route to the synthesis of organoboranes. Finally, it was demonstrated that diborane, generated through the reaction of sodium borohydride with boron trifluoride etherate in diglyme, adds to carbon-carbon double and triple bonds, carbon-oxygen double bond and carbon-nitrogen double and triple bonds to give organoboranes in almost quantitative yields (Scheme 1).[4,6] The behaviour of various types of hydroborating agents towards a number of substrates has recently initiated interesting studies on stereochemistry and reaction mechanism.

Scheme 1

$$3\ NaBH_4 + 4\ BF_3 \longrightarrow 3\ NaBF_4 + 2\ B_2H_6$$
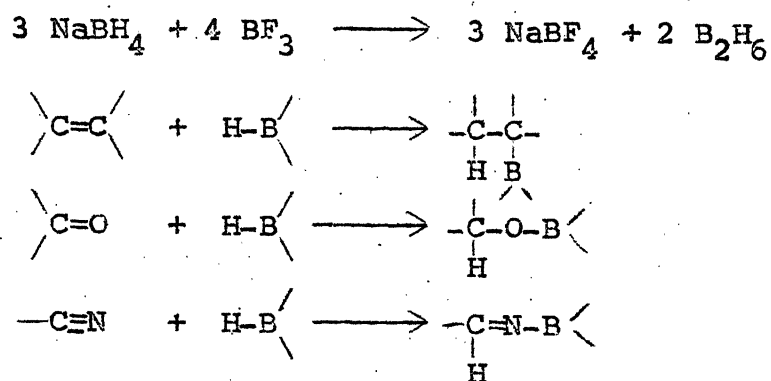
I.2.1 Selective Hydroborating Agents

The hydroboration of an olefin affords monoalkyl, dialkyl or trialkylborane, depending upon the structure of the olefin. The intermediate organoboranes act as a monohydroborating or dihydroborating reagent subject to the availability of $>$B-H linkage present in the borane. Hydroboration of olefins, such as 2-methyl-2-butene, cyclohexene, 1-methylcyclohexene and α-pinene, was observed to provide dialkylboranes (Scheme 2).[7]

Scheme 2

$(CH_3)_2C=CH-CH_3$ + (BH_3) $\longrightarrow$ $\left[(CH_3)_2CH-\overset{|}{C}H-CH_3\right]_2BH$

Disiamylborane (DAB)

Dicyclohexylborane (DCB)

Bis (trans-2-methyl-cyclohexyl)borane (BMCB)

Diisopinocamphenyl-borane (DICB)
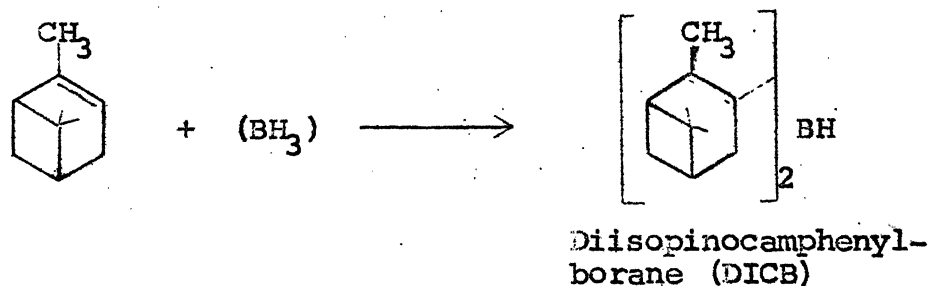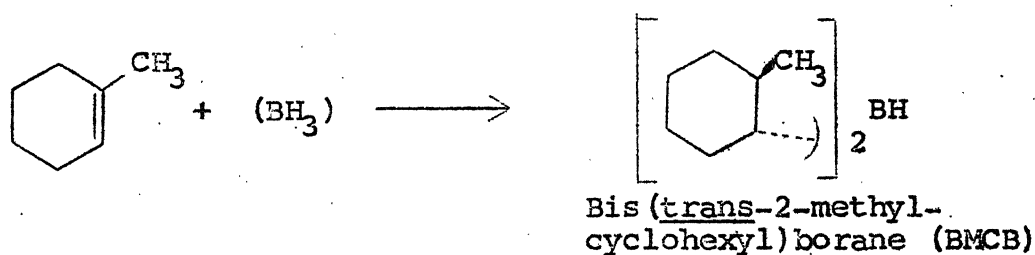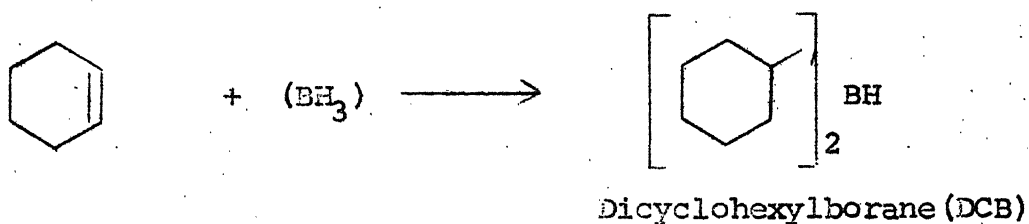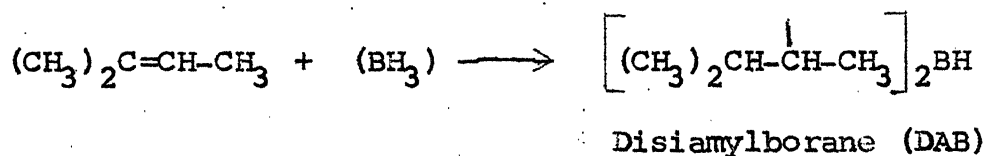
The disiamylborane (DAB) obtained from 2-methyl-2-butene has proved to be of major value as a selective hydroborating agent.[7,8] The other dialkylboranes (DCB,BMCB and DICB) are also useful as hydroborating agents in providing a steric control over hydroboration as well as high selectivity in the competitive hydroboration of two olefins of different structures.[9] For example, the hydroboration of styrene with diborane proceeds with 81% attack of boron at the β -position whereas DAB provides 99% attack at the β -position (Scheme 3). Diisopinocamphenylborane

Scheme 3

$$C_6H_5-CH=CH_2$$

$$\begin{array}{cc}\uparrow & \uparrow \\ \underline{\hspace{1cm}} \end{array} \text{—— Attack of boron with } B_2H_6$$

19% 81%

1% 99% ———— Attack of boron with DAB
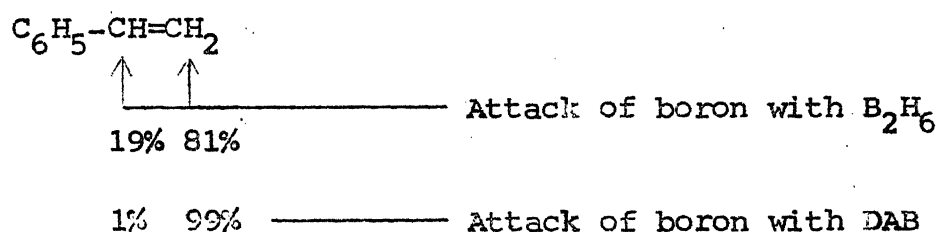
is an optically active hydroborating agent and achieves remarkable asymmetric syntheses.[10]

More recently, 9-borabicyclo(3.3.1)nonane[11] (9-BBN) obtained by the hydroboration of 1,5-cyclooctadiene has been shown to be quite comparable to DAB as far as selectivity is concerned (Scheme 4).

Scheme 4

9-Borabicyclo(3.3.1)-
nonane (9-BBN)
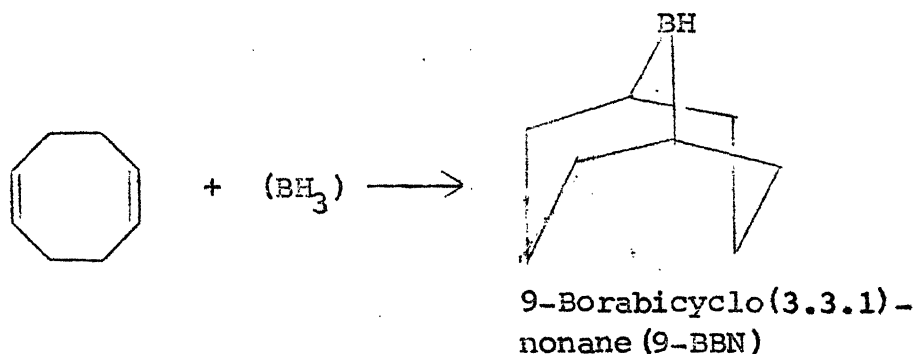
Hydroboration of a more hindered olefin, 2,3-dimethyl-2-
butene, with diborane readily proceeds to the monoalkylborane
stage, giving rise to 2,3-dimethyl-2-butylborane[7,12,13] (thexyl-
borane). Thexylborane is an unique reagent for cyclic hydro-
boration of dienes leading to the formation of boron hetero-
cyclic compounds (Scheme 5). Several other hydroborating reagents
like dialkoxyborane,[14] butylthioborane,[15] monochloro- and dichlo-
roborane,[16-18] and boron aluminium alcoholate[19] have been used
as hydroborating agents.

Scheme 5

$$(CH_3)_2C=C(CH_3)_2 \ + \ (BH_3) \ \longrightarrow \ \vdash\!\!\!\!+\!\!\!\!-BH_2$$

Thexylborane
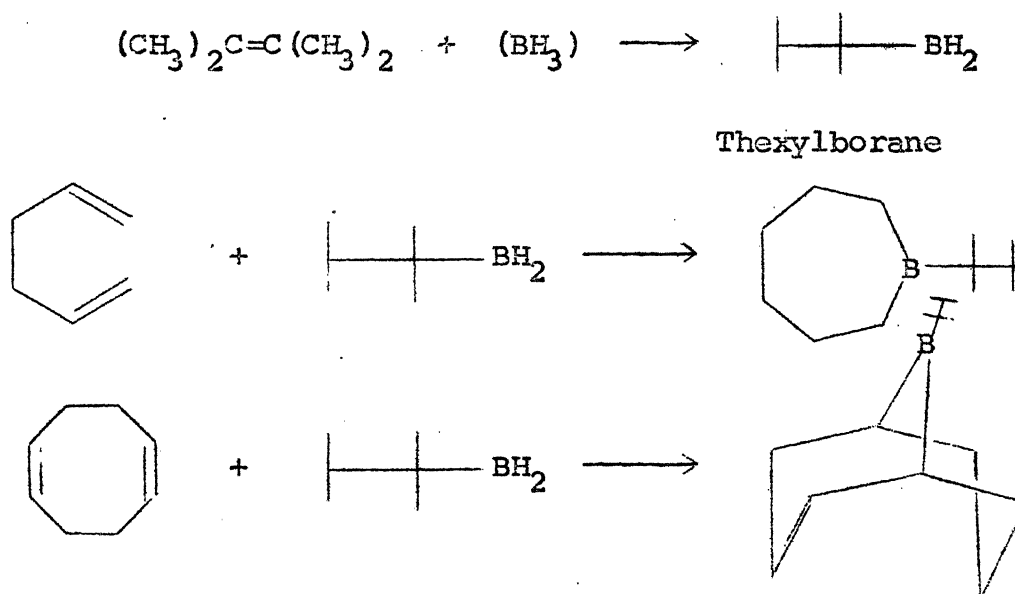
I.2.2 Mechanism and Stereochemistry

The hydroboration of 1-methylcyclohexene followed by oxidation with hydrogen peroxide in the presence of alkali affords pure trans-2-methylcyclohexanol (Scheme 6). Since the hydrogen peroxide oxidation is essentially quantitative and possesses remarkable specificity for the boron-carbon bond, the hydroboration reaction must involve a cis addition of the boron-hydrogen bond to the double bond of the cyclic olefin through a simple four centre cyclic transition state as shown in Scheme 6.

Scheme 6
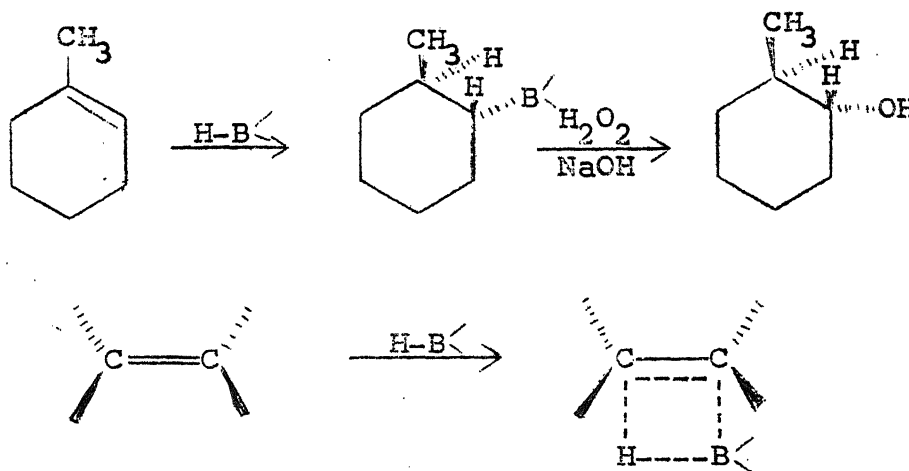
Therefore, it follows that the overall hydration proceeds as an anti-Markownikoff's cis-hydration of the double bond, pre-ferentially from the less hindered site of the double bond. This generalization is now supported by a large number of independent observations.[20]

I.2.3 __Directive Effects__

The mode of addition of $\rangle$B-H moiety to the unsaturated linkage is very sensitive to steric and electronic factors. These effects will be dealt under two headings: (i) attack of boron controlled by steric factor, and (ii) attack of boron controlled both by electronic and steric factors.

(i) __Attack of Boron Controlled by Steric Factor__[7]: The terminal olefins on hydroboration give mainly terminal organo-boranes, while 1,1-disubstituted alkenes give exclusively organoborane corresponding to terminal attack of boron. These results clearly show that in the case of disubstituted terminal olefins, the directive effect of the two substituents is overwhelming and it results in almost complete addition of boron to the terminal position of the carbon-carbon double bond. In disubstituted internal olefins, boron adds farther from the bulky substituent and in trisubstituted olefins secondary position is favoured over tertiary by boron (Scheme 7). Directive effects controlled by steric factors of the bulk of the hydroborating agents have been summarized in Schemes 3 and 4. It is interesting to observe that based on the study of the steric effects of variously positioned alkyl substituents in the cyclohexene system, Pasto and Klein[21,22] have developed a method for the convenient synthesis of __trans,trans-di-t-butylcyclohexanol__.

(ii) __Attack of Boron Controlled by Electronic and Steric Factors__: The role of electronic effects of various substituents in influencing the direction of addition of the

Scheme 7

RCH=CH$_2$

$\uparrow$ $\uparrow$

6-7% 93-94% ————— Attack of born of diborane

RR'C=CH$_2$

$\uparrow$ $\uparrow$

1-2% 98-99% ————— Attack of boron of diborane

RR'C=CHR"

$\uparrow$ $\uparrow$

2% 98% ————— Attack of boron of diborane

RCH=CHR'

$\uparrow$ $\uparrow$

45% 55% ————— Attack of boron of diborane
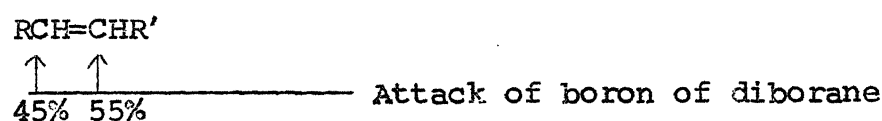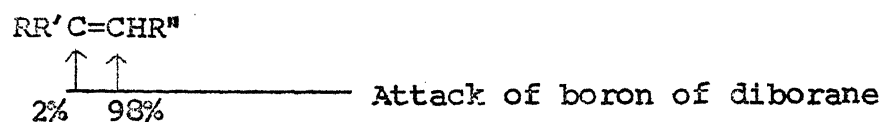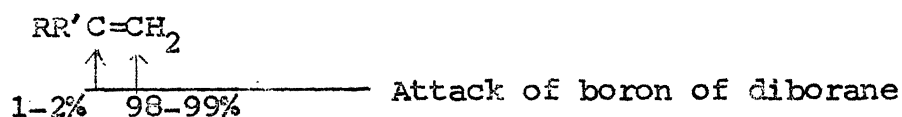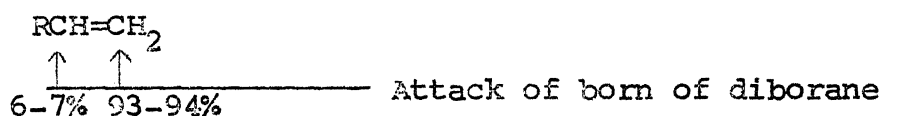
R, R', R" are n-alkyl moieties

$>$B-H moiety to the carbon-carbon double bond has been studied

critically by Brown and Sharp[23] in a number of substituted

styrenes. Clearly, in all the cases the steric factor predomi-

nates, whereas electronic factor varies through different substi-

tuents at ortho, meta and para position of the benzene ring.

All the available evidences indicate that the addition of $>$B-H

moiety involves a four-centre transition state. A group with

a powerful electron releasing effect would be expected to favour

the transition state (A) causing decrease in addition to the

α-position. On the contrary, a group with a powerful electron

withdrawing effect should favour the transition state (B)
(Scheme 8).

<p align="center">Scheme 8</p>

$$X-C_6H_4-\overset{\delta\oplus}{CH}---\overset{\delta\ominus}{CH_2}$$
$$H---B$$
$$\overset{\delta\ominus}{} \quad \overset{\delta\oplus}{}$$

$$X-C_6H_4-\overset{\delta\ominus}{CH}---\overset{\delta\oplus}{CH_2}$$
$$B---H$$
$$\overset{\delta\oplus}{} \quad \overset{\delta\ominus}{}$$
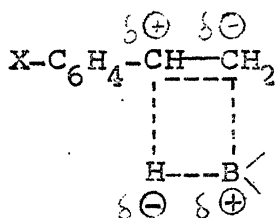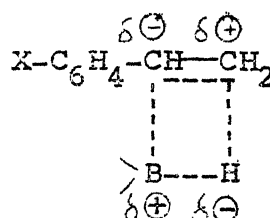
<p align="center">Transition state (A)   Transition state (B)</p>

Similarly, directive effects in vinyl derivatives,[24] cyclopropyl,[25] 3-cyclopentenyl,[26] 2-butenyl,[27] 3-butenyl,[28] and alkyl derivatives containing representative substituents[29] have been studied by Brown and coworkers. The effects of carboxylate[30] and hydroxyl[31] groups in the hydroboration of cyclohexene ring have also been examined. Seyfeath and coworkers[32,33] have dealt with the directive effects in the hydroboration of allyl-trimethylsilane and vinylmethylsilane. This has been utilized in the synthesis of cis- and trans-trimethylsilylcyclohexanol.[34]

I.2.4 Hydroboration of Conjugated and Unconjugated Dienes

Despite the relative recent origin of hydroboration reaction, the subject has become so wide that it is very difficult to survey here all the developments of interest in this field. So we restrict ourselves to the study of hydroboration of conjugated and unconjugated dienes.

I.2.5   Hydroboration of Acyclic Dienes

Hydroboration of 1,3-, 1,4- and 1,5-dienes usually gives cyclic organoboranes. Such organoboranes were first reported by Koster,[35,36] who obtained them by thermolysis of trialkyl organoboranes.[36] Oxidation of cyclic organoboranes with alkaline hydrogen peroxide gives rise to glycols.[7] In some cases, the monohydroboration of dienes can be controlled to produce unsaturated alcohols.

The hydroboration of olefins proceeds quantitatively to the organoborane. However, the extension of hydroboration to dienes mainly involves two problems.[7] First, the reaction of difunctional diene with polyfunctional diborane molecule results in the formation of polymeric products, which do not exhibit the customary behaviour of organoboranes. Second, the conjugated dienes are less reactive towards simple addition reaction as compared to the related olefins. Consequently, the controlled monohydroboration of such dienes is very difficult.

Hydroboration of a number of representative acyclic dienes (1,3-butadiene, substituted 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene) has been thoroughly investigated using borane,[37-41] thexylborane,[12,13] disiamylborane[42], tetraethyldiborane[36] and trimethylamine-t-butylborane[43] in solution and in vapour phase.[44] The intermediate organoboranes on oxidation with alkaline hydro--gen peroxide yield isomeric diols, the distribution of which depends on the condition of hydroboration and the nature of the

olefin and hydroborating agent.(Scheme 9).

<div align="center">Scheme 9</div>

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2 \xrightarrow[H_2O_2.NaOH]{BH_3-THF}$$

$$HO-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-OH \quad (87\%)$$

$$HO-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-OH \quad (13\%)$$

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-C=CH_2 \xrightarrow[H_2O_2.NaOH]{BH_3-THF} HO-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-OH$$

$$HO-CH_2(CH_2)_3-CH_2-OH \quad + \quad HO-CH_2-(CH_2)-\overset{\overset{\displaystyle CH_3}{|}}{CH}-OH$$

BH₃-THF	(38%)	(62%)
⊢ BH₂	(38%)	(62%)
Sia₂BH	(85%)	(15%)

$$HO-CH_2-(CH_2)_4-CH_2-OH \quad + \quad HO-CH_2-(CH_2)_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-OH$$

BH₃-THF	(69%)	(31%)
Sia₂BH	(93%)	(7%)
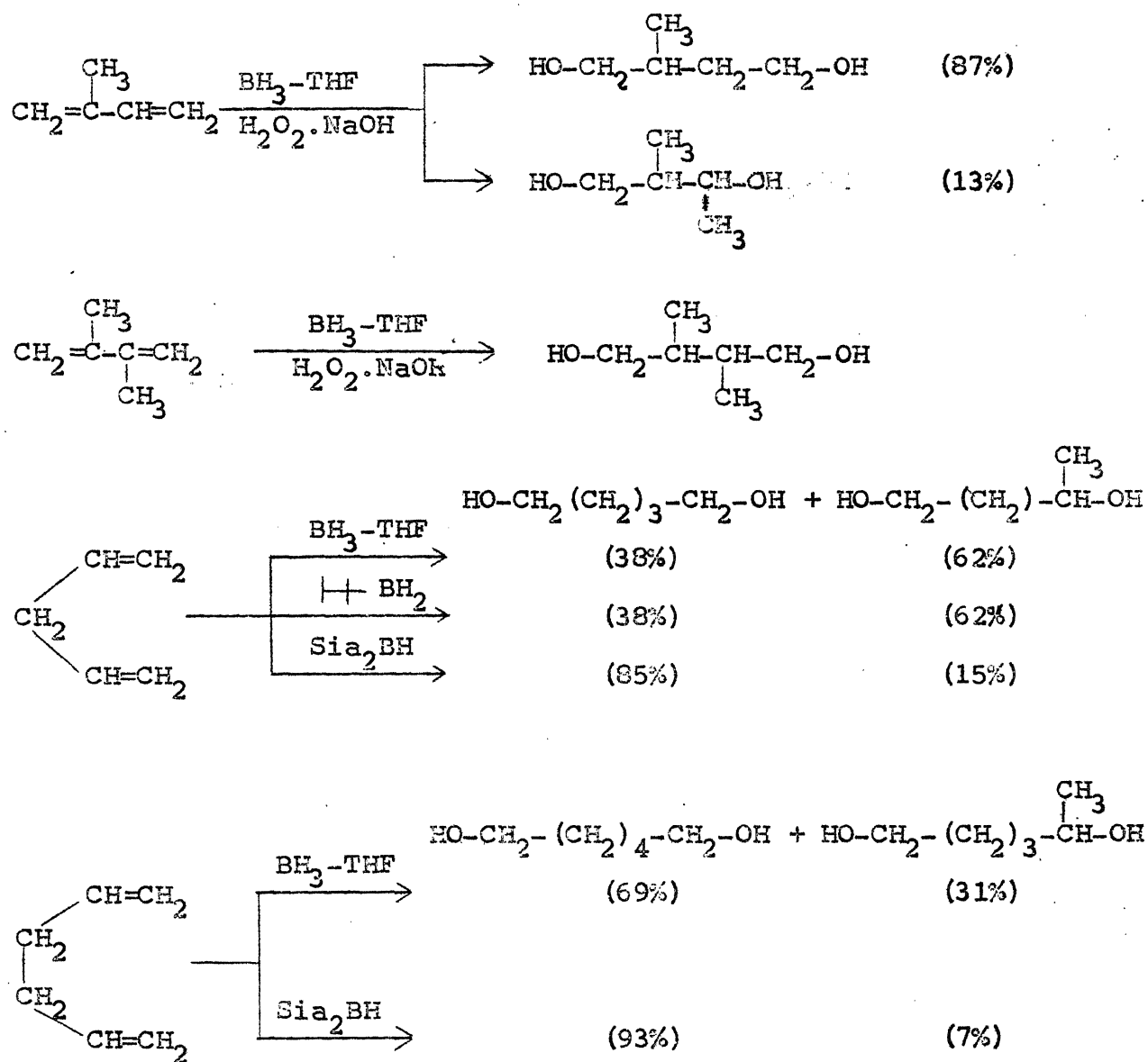
With disiamylborane as the hydroborating agent, more selectivity is observed.[42] Borane-tetrahydrofuran and thexylborane give nearly the same distribution of diols.[12] This is due to the

fact that both the reagents favour the intramolecular addition of second boron-hydrogen bond to the double bond of the mono-hydroborated diene, leading to the formation of cyclic organo-boranes. The high yield of 1,4-diol from 1,5-pentadiene is also attributed to the prominent tendency toward cyclization. This observation argues against the thermodynamic control of the product formation in hydroboration of dienes under the conditions used.[40] The position of the boron atom in the thermal rearrangement of bis(1-boracycloalkyl)alkane prepared by hydroboration of a diene with BH_3-THF (3:2) is dictated by the size of hetero ring. It has been established that boracyclohexane (borinane) is more stable than boracyclopentane or boracycloheptane (Scheme 10).

Scheme 10
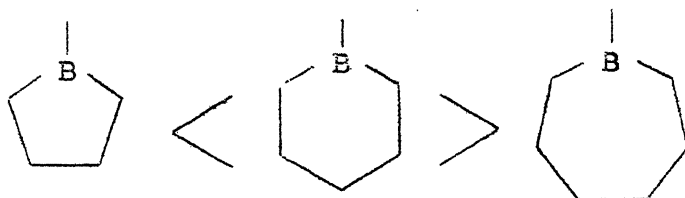
The use of thexylborane as hydroborating agent avoids the formation of insoluble polymeric organoboranes. B-alkylboracyclo-alkanes are synthesized using trimethylamine-t-butylborane[36] and tetraalkyldiborane[43] (Scheme 11).

Hydroboration of 1,3-butadiene results in the formation of a mixture of 1,3- and 1,4-butane diols. The relative yield of the diols is markedly influenced by reaction conditions.

Scheme 11

$$\text{(cyclopentadiene)} + \underset{}{\overset{- \quad +}{t\text{-BuBH}_2\text{-N(CH}_3)_3}} \xrightarrow{65^0} \underset{\overset{\big|}{B}}{\overset{t\text{-Bu}}{\text{(cyclohexane ring)}}} + (CH_3)_3N$$

$$H_3C\text{-(diene)} + (C_2H_5)_4B_2H_2 \longrightarrow \underset{H_3C}{\overset{C_2H_5}{\overset{\big|}{B}}\text{(ring)}} + (C_2H_5)_3B$$
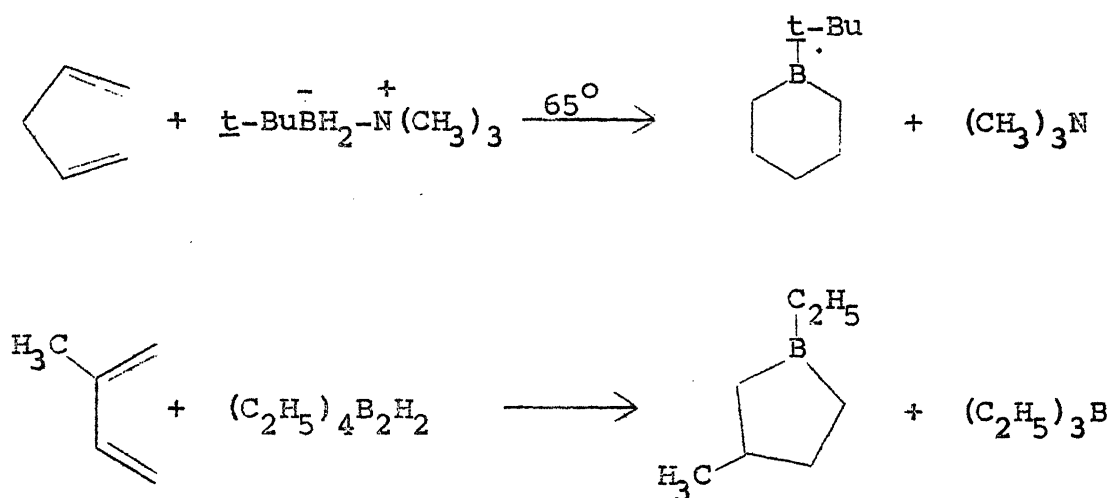
Addition of borane in tetrahydrofuran to butadiene in the same sol-
vent results in rapid utilization of the available hydride and
gives 1,3- and 1,4-butane diols in the ratio 24:76. On the other
hand, the addition of butadiene to borane in tetrahydrofuran is
relatively slow at the later stage and results in the formation
of more 1,3-diol.[7,37] The slow reaction is due to the difficulty
experienced by the butadiene molecule in approaching the resi-
dual boron-hydrogen bond entangled within the three dimensional
net-like structure in the polymer.

I.2.6 Nature of the Organoboranes from the Hydroboration of
       1,3-Butadiene

Hydroboration of 1,3-butadiene has revealed a number
of highly interesting and unusual features. The reaction between
1,3-butadiene and diborane in 2:1 molar ratio yields a distilla-
ble organoborane[38] which exhibits high stability towards alcohols,

olefins and oxidizing agents. Koster has proposed its structure to be that of bis-borolane[38,39] (1) (Scheme 12). However, an alternate structure, 1,6-diboracyclodecane (2) stabilized by transannular boron-hydrogen bridge has been proposed by Brown and Breuer[46] to account for the observed unusual properties of this organoborane. Based on the studies of hydrogen bridge cleavage reaction, and NMR, Young and Shore[47] have suggested the structure 4 to the product obtained from 1,3-butadiene and diborane (1:1 molar ratio) rather than 3 as proposed by Koster,, (Scheme 12).

<u>Scheme 12</u>
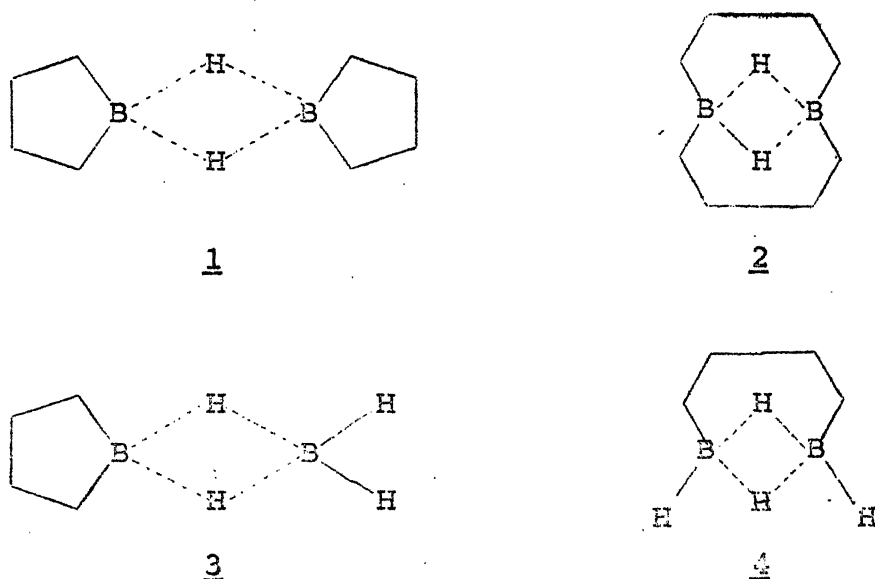
The organoboranes from 1,3-butadiene and borane in tetrahydrofuran in stoichiometric ratio consist of monomeric dumb-bell shaped compounds, 1,3- and 1,4-diborabutanes[38-40,48] (5 and 6) in the ratio 7:3, the thermal isomerization of which gives

gem-dibora compound (7) as the major product[49] (Scheme 13).

Scheme 13

$$3 \ CH_2=CH-CH=CH_2 \ + \ 2(BH_3) \ \longrightarrow$$
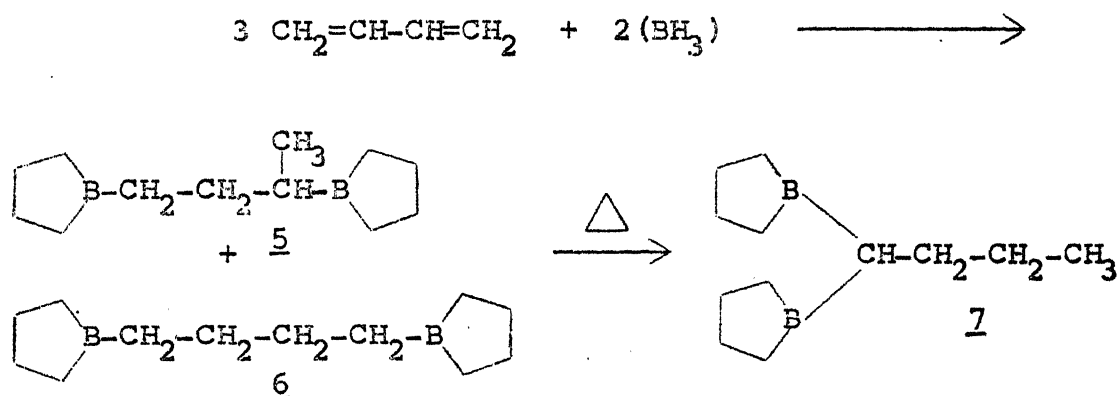
1:1 Hydroboration product is found to be almost entirely poly-meric and essentially free from 3:2 adduct (5 and 6) even when BH_3-THF is added to 1,3-butadiene. The formation of polymer has been explained by Brown and his coworkers[49,50] via 3:2 adducts as intermediates. The reaction of 3:2 adducts (5 and 6) with an equimolar quantity of borane yields a statistical mixture of 8 (50%), 9 (25%),and 5 and 6 (25%) (Scheme 14).

Scheme 14
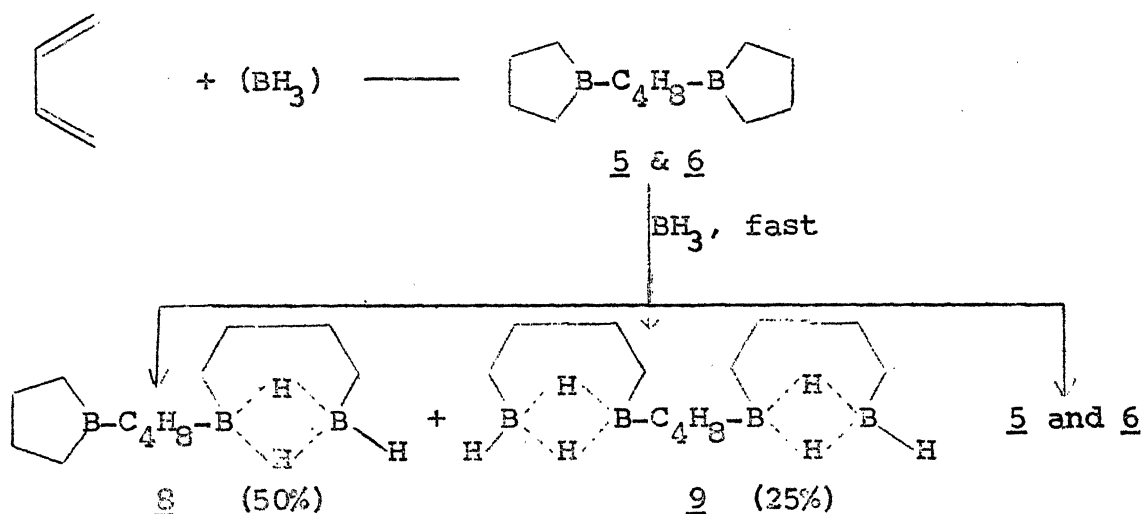
Absence of the stable dimer[46] (2) excludes the inter-
mediacy of 4 since Young and Shore have reported that 4 reacts
with 1,3-butadiene to form 2 as the sole product and 2 itself
does not react with borane or butadiene at any appreciable rate
at room temperature.[47] Hydroboration of 1,3-butadiene with
borane in tetrahedrofuran in 3:4 molar ratio yields 9 as the
distinct product via 3:2 adducts (5 and 6) and use of any
excessive quantity of BH_3-THF does not significantly affect the
nature of reaction.

The course of the reaction of 1,3-butadiene with borane
in tetrahydrofuran[49] in various stoichiometric ratios is summa-
rized in Scheme 15.

Scheme 15

1,3-Butadiene/borane	Product

3/2

$$B-C_4H_8-B$$

5 and 6

1/1

$$\left[-B \cdots \overset{H}{\underset{H}{\cdots}} B-C_4H_8 \right]_n^-$$

3/4

$$H-B \overset{H}{\underset{H}{\cdots}} B-C_4H_8-B \overset{H}{\underset{H}{\cdots}} B-H$$
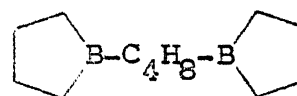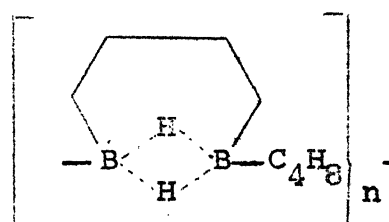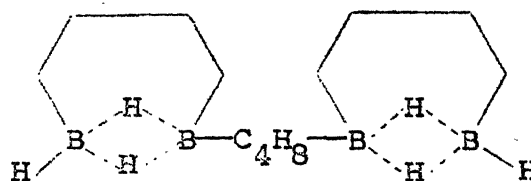
9

I.2.7 Hydroboration of Cyclic Dienes

cis,cis-1,5-Cyclooctadiene preferentially undergoes dihydroboration to give bicyclic organoborane,[37,42] which is also formed by the pyrolysis of tri-cyclooctylborane.[51] Gardner and coworkers[52] studied the hydroboration of cis,cis-1,5-cyclooctadiene using externally generated diborane and isolated cis-1,5-cyclooctane diol as the major product, (Scheme 16).

Scheme 16
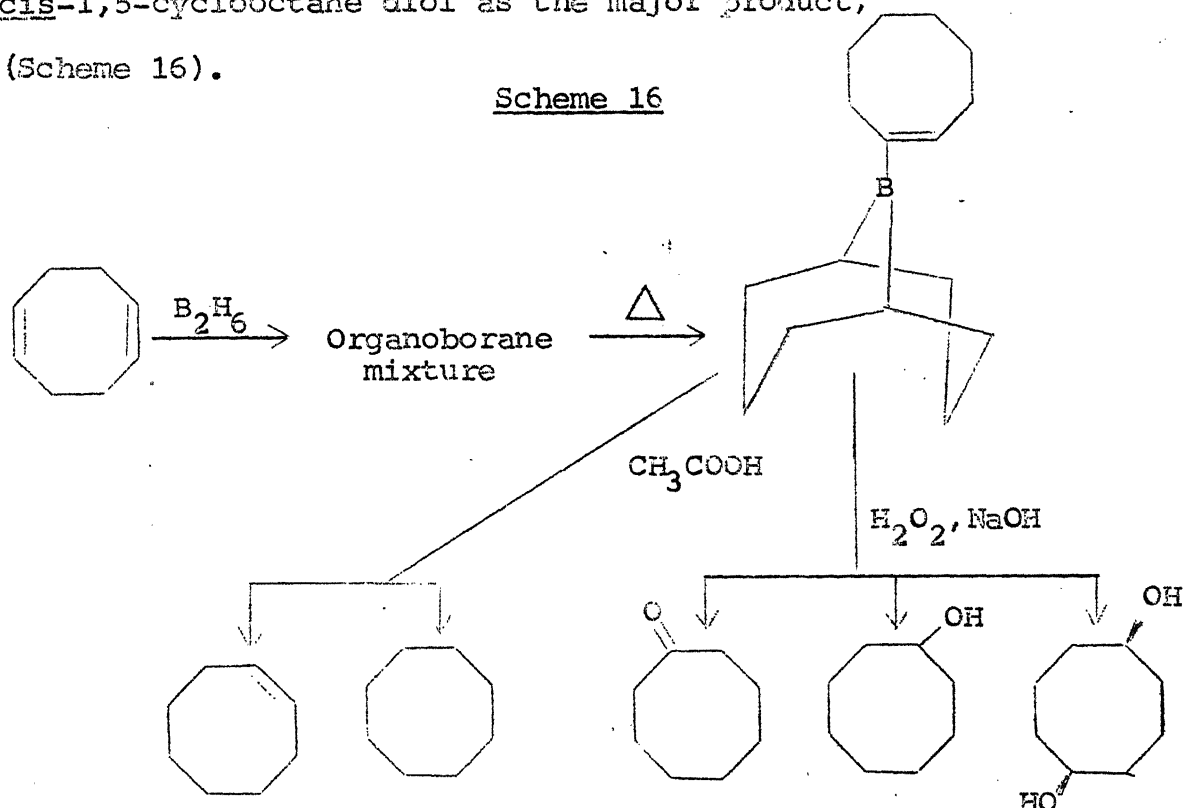
Later Brown[53] isolated the organoborane using borane solution in tetrahydrofuran and characterized it as 9-borabicyclo(3.3.1)-nonane. Oxidation of the isomerized organoborane gives cis-1,5-cyclooctane diol. While the one without isomerization gives a mixture of cis-1,4- and 1,5-cyclooctane diols in which the 1,5-diol predominates (Scheme 17).

Scheme 17
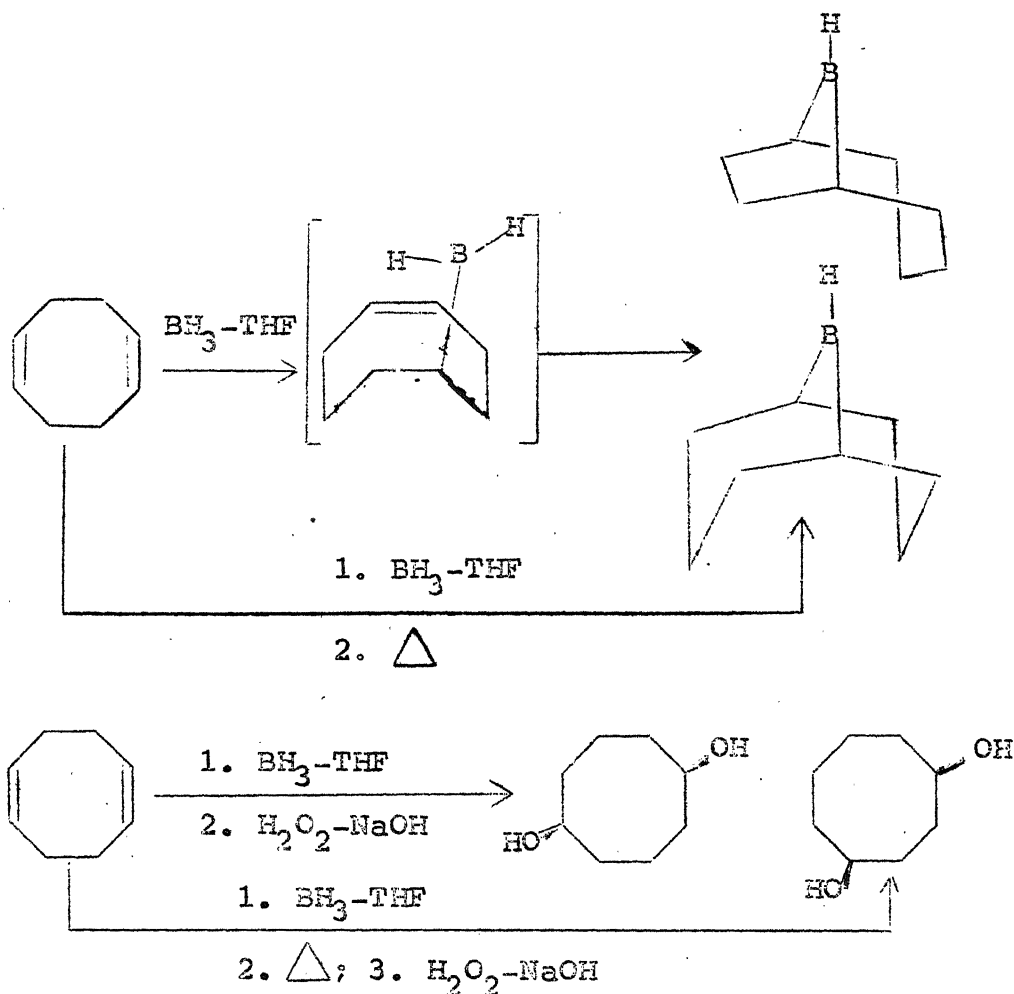
Koster has isolated B-ethyl-9-borabicyclo(3.3.1)nonane from cis,cis-1,5-cyclooctadiene and tetraethyldiborane (Scheme 18).[36]

Scheme 18
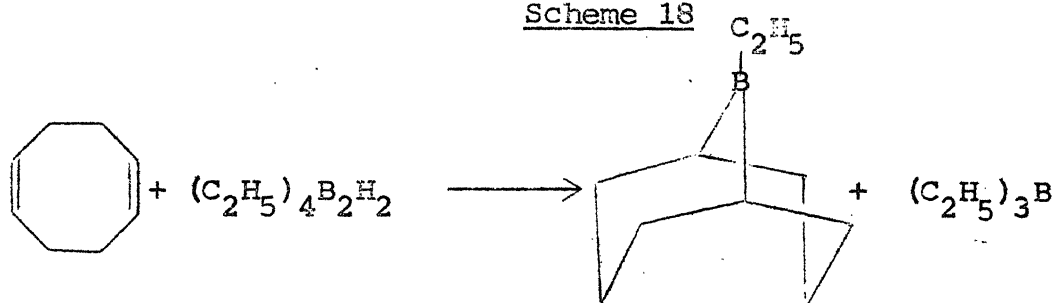
D(+)-Limonene and vinylcyclohexene[54] undergo cyclic hydroboration with thexylborane[13] to give bicyclic organobranes

which could be utilized either in the stereospecific synthesis
of diols or bicyclic ketones (Scheme 19). However, cyclic dienes
such as 1,3-cyclohexadiene[7] cyclopentadiene[41] and bicyclohepta-
diene do not undergo cyclic hydroboration (Scheme 19).

<u>Scheme 19</u>
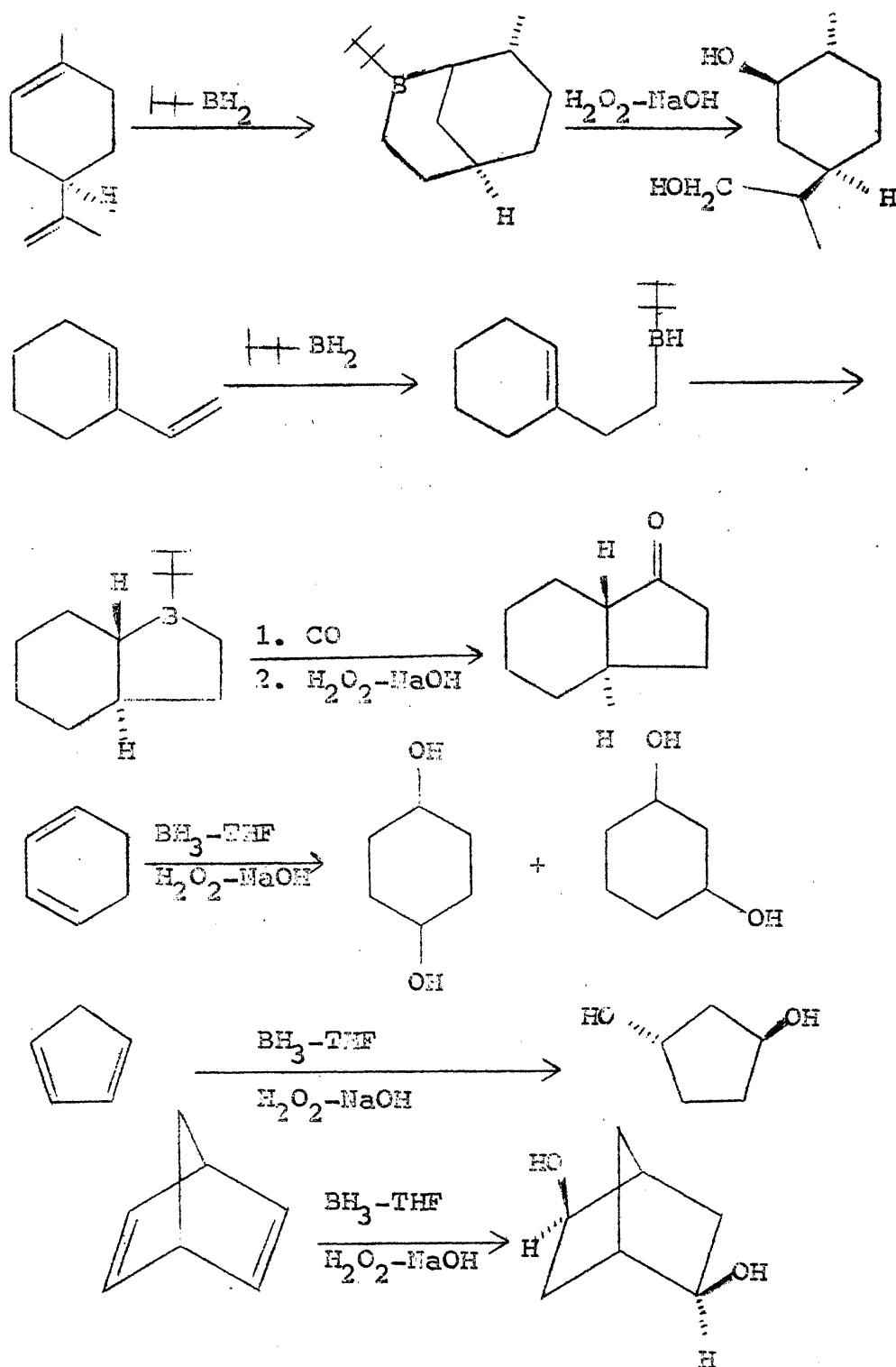
I.2.8 Monohydroboration of Dienes

Monohydroboration of unconjugated acyclic dienes with diborane is more favoured than conjugated dienes.[55-57] For example, 1,5-hexadiene yields very nearly the statistical distribution of 50% mono- and 25% di-hydroboration products.[7,37,42] In the case of cyclic dienes, monohydroboration is more favoured as compared to acyclic dienes, whether the diene is conjugated or not. However, there is competition between the two hydroboration stages. Unsaturated alcohols have been obtained by the monohydroboration of cyclopentadiene,[58] 1,3-cyclohexadiene[7] and bicycloheptadiene[7] in reasonable yield (35-70%) with diborane (Scheme 20).

<p align="center">Scheme 20</p>
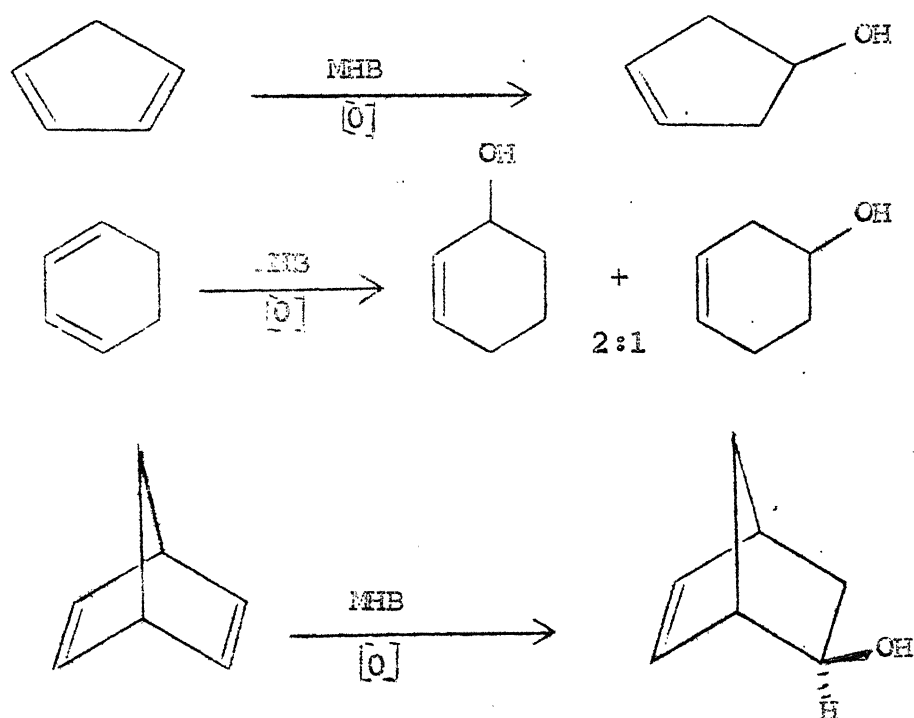
Yield of these unsaturated alcohols has been improved by using disiamylborane[55-57] as hydroborating agent (Scheme 21).

Scheme 21

$$CH_2=CH-CH=CH-CH_3 \xrightarrow[H_2O_2-NaOH]{Sia_2BH} CH_3-CH=CH-CH_2-CH_2OH$$

$$\begin{array}{c} CH_2-CH=CH_2 \\ | \\ CH_2-CH=CH_2 \end{array} \xrightarrow[H_2O_2-NaOH]{Sia_2BH} \begin{array}{c} CH_2-CH=CH_2 \\ | \\ CH_2-CH_2-CH_2OH \end{array}$$

$$\xrightarrow[H_2O_2-NaOH]{Sia_2BH}$$

1,9-Cyclohexadecadiene
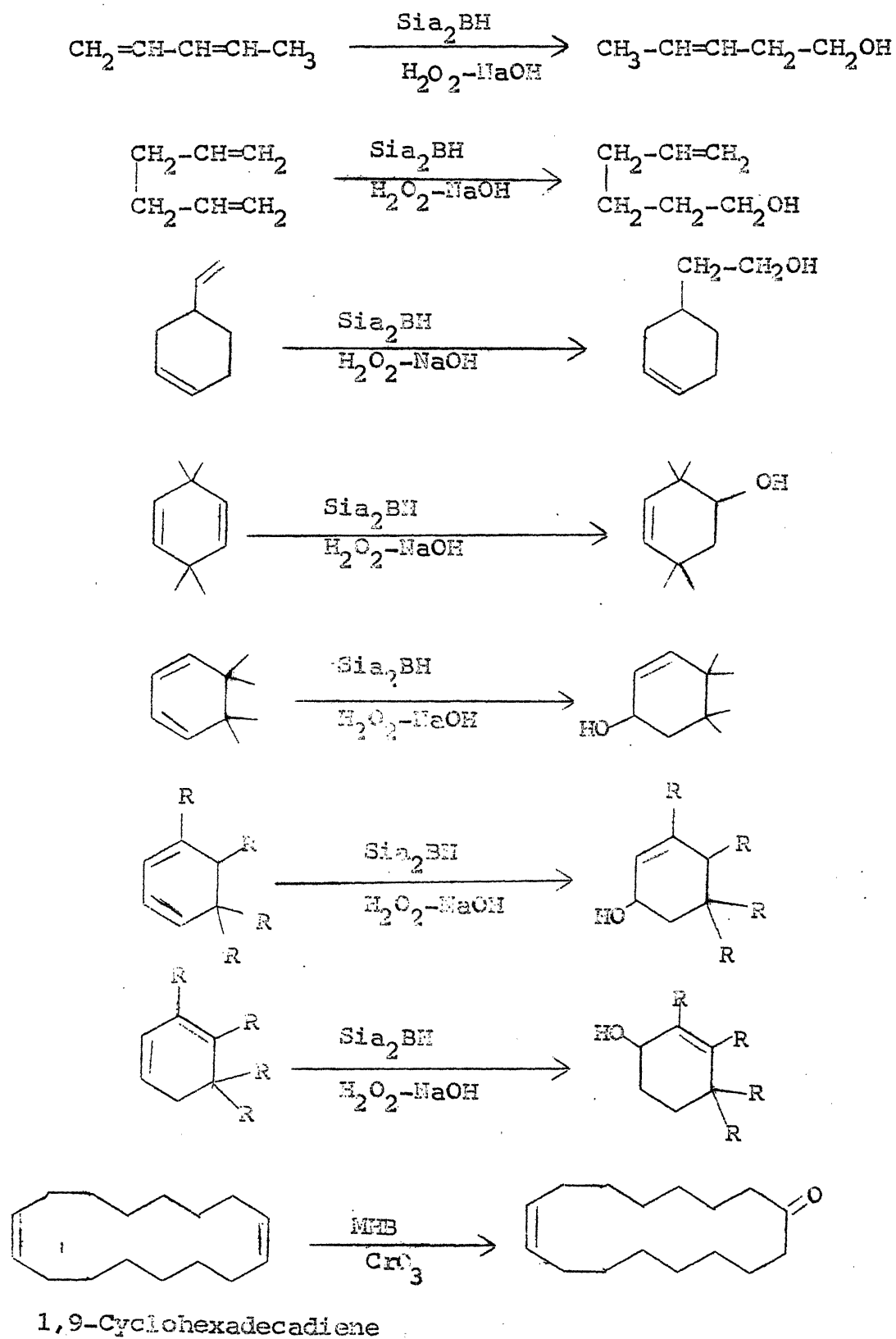
However, cis,cis-1,5-cyclooctadiene undergoes dihydroboration even with disiamylborane. The decreased reactivity of this diene over olefin may be due to transannular conjugation of the two double bonds.

The organoboranes as synthetic intermediates have created immense interest since the discovery of the reaction of diborane with alkenes and related unsaturated compounds.[7] The observation that the reaction of cis,cis-1,5-cyclooctadiene with borane in tetrahydrofuran can be controlled to provide a convenient synthesis of 9-borabicyclo(3.3.1)nonane which on oxidation yields cis-1,5-cyclooctane diol,[53] has prompted us to investigate the synthetic utility of this valuable reaction. Therefore, we undertook the investigation of the cyclic hydroboration of medium ring dienes in eight-, nine and ten-membered rings.

I.3 RESULTS AND DISCUSSION

The medium-ring dienes, cis,cis-1,3-cyclooctadiene (10), cis,cis-1,5-cyclooctadiene (11), cis,trans-1,5-cyclodecadiene (17) and cis,cis-1,6-cyclodecadiene (18) used in this investigation were obtained from commercial firms. The other medium-ring dienes, cis,cis-1,3-cyclononadiene[62] (12), cis,cis-1,4-cyclononadiene[64] (13), cis,cis-1,5-cyclononadiene[65] (14), cis,cis-1,3-cyclodecadiene[68] (15) and cis,cis-1,4-cyclodecadiene[68] (16) were synthesised by known procedures as described in the literature (Scheme 22).

Scheme 22

10   11   12

13   14   15

16   17   18
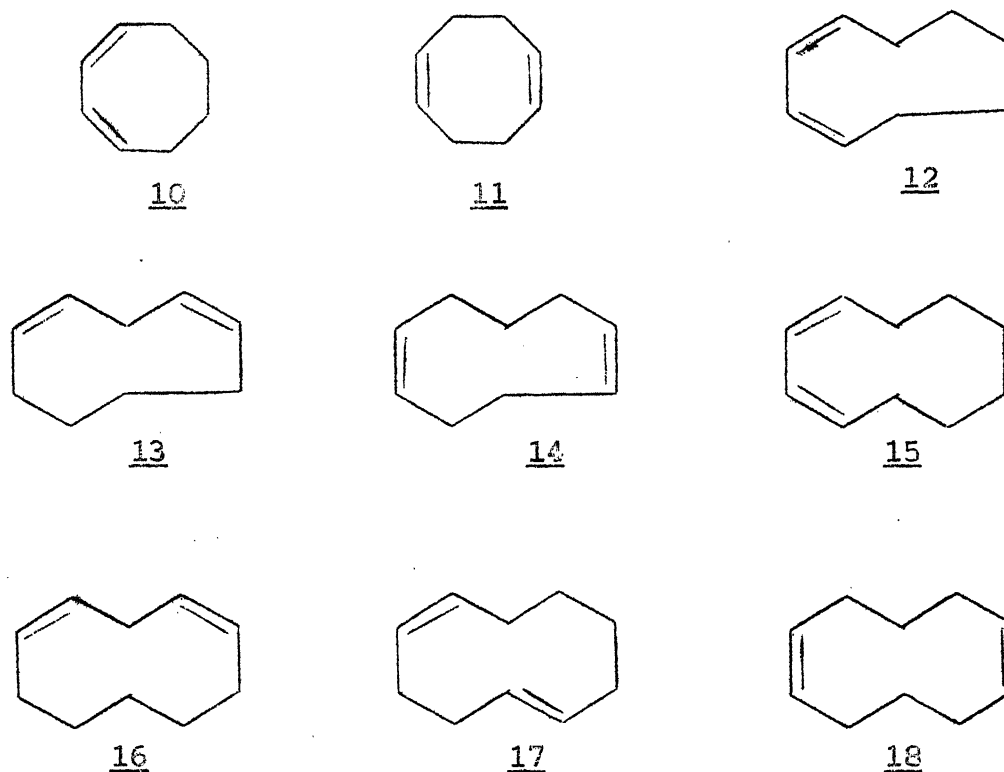
cis,cis-1,3-Cyclononadiene (12) was synthesized from

1,2-cyclononadiene (21), which in turn was obtained from

cis-cyclooctene (19) by a two-step sequence.[59-61] The

1,2-cyclononadiene (21) obtained was found to be pure as

analysed by GLC. All the physical and spectral properties

were in agreement with the reported values. The treatment of

1,2-cyclononadiene (21) with hydrogen bromide in acetic acid

in 1:1 mole ratio at 10-15° gave 3-bromocyclononene (22)

in 85% yield. The product had identical properties as reported

in the literature. Dehydrobromination[62] of 3-bromocyclononene

(22) by potassium t-butoxide in DMSO for 5 min at room tempera-

ture gave cis,cis-1,3-cyclononadiene (12) in .72% yield

(Scheme 23). The product (12) corresponded in all respects

(GLC, IR and NMR) with an authentic sample of cis,cis-1,3-

cyclononadiene[63] (12).

Scheme 23
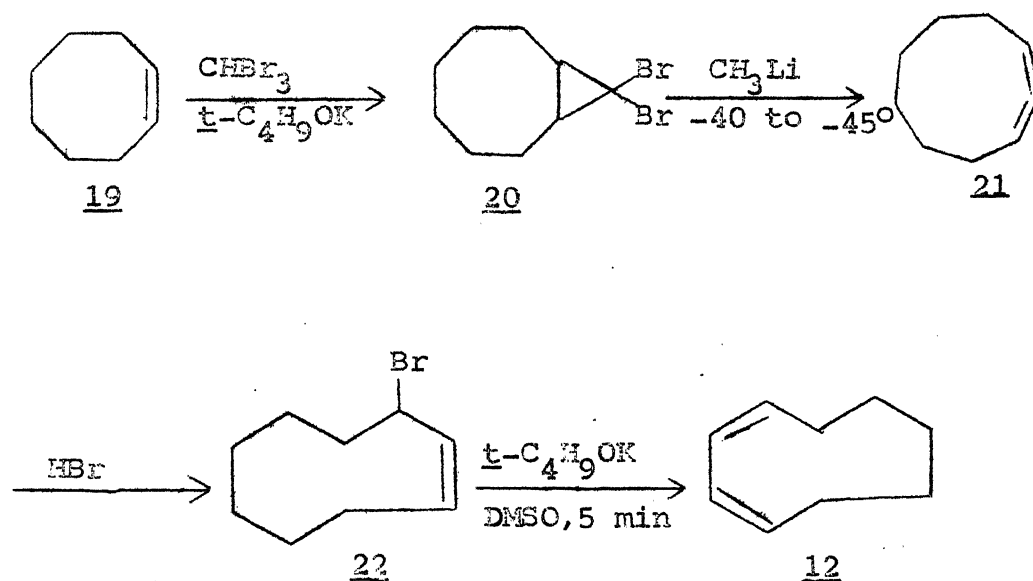
cis,cis-1,4-Cyclononadiene (13) was prepared by pyrolysis[64]

of bicyclo(6.1.0)non.-2-ene[61] (24) which was synthesized in two

steps starting from cis,cis-1,3-cyclooctadiene (10) (Scheme 24).

The IR spectrum of 13 showed bands only for cis double bond.

GLC analysis indicated it to be pure and the structure was

confirmed by NMR.

The synthesis of the medium-ring diene, cis,cis-1,5-

cyclononadiene (14) was achieved by two-step sequence[65] starting

Scheme 24
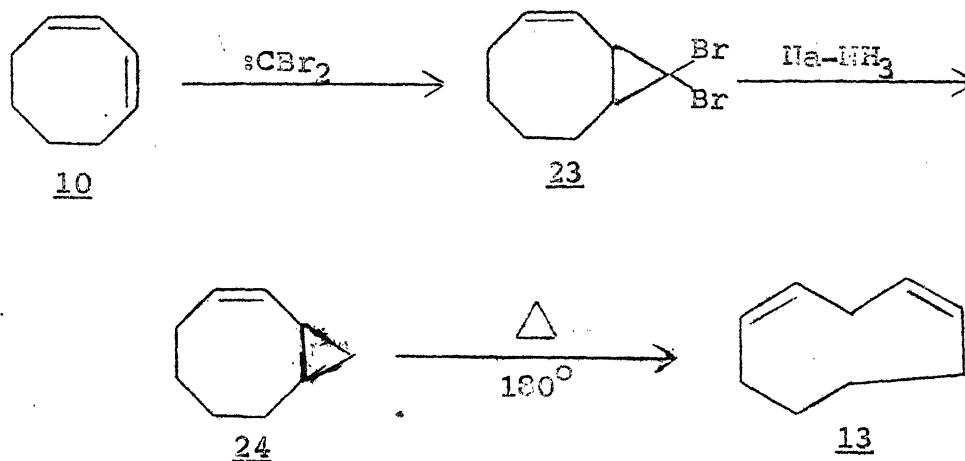
from readily available cis,cis-1,5-cyclooctadiene (11)
(Scheme 25). 1,2,6-Cyclononatriene (25) was prepared by the
reaction of carbon tetrabromide and methyllithium with cis,cis-
1,5-cyclooctadiene (11) at about -70°. Reduction of 1,2,6-cyclo-
nonatriene (25) with sodium in liquid ammonia provided 84% of
cis,cis-1,5-cyclononadiene (14) which showed identical IR and
GLC retention time with an authentic sample.[66]

Scheme 25
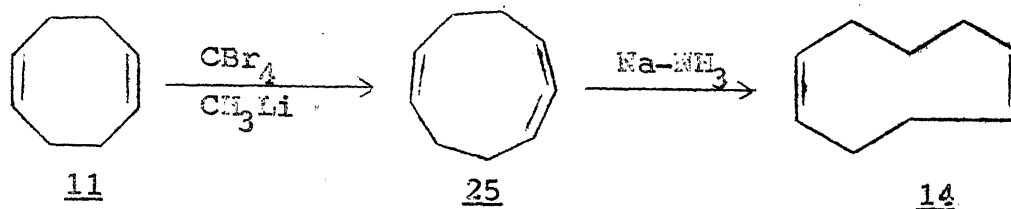
Isomerization[67] of 1,2-cyclodecadiene (27) with potassium t-butoxide in DMSO for 12 hr at room temperature gave a 4:1 mixture of cis,cis-1,3- (15) and cis,cis-1,4-cyclodecadiene (16) Pure compounds were obtained by preparative GLC and characterized using authentic samples.[68] 1,2-Cyclodecadiene (27) was made from cis-cyclononene (26) by the usual two-step synthesis (Scheme 26).

<div align="center">Scheme 26</div>
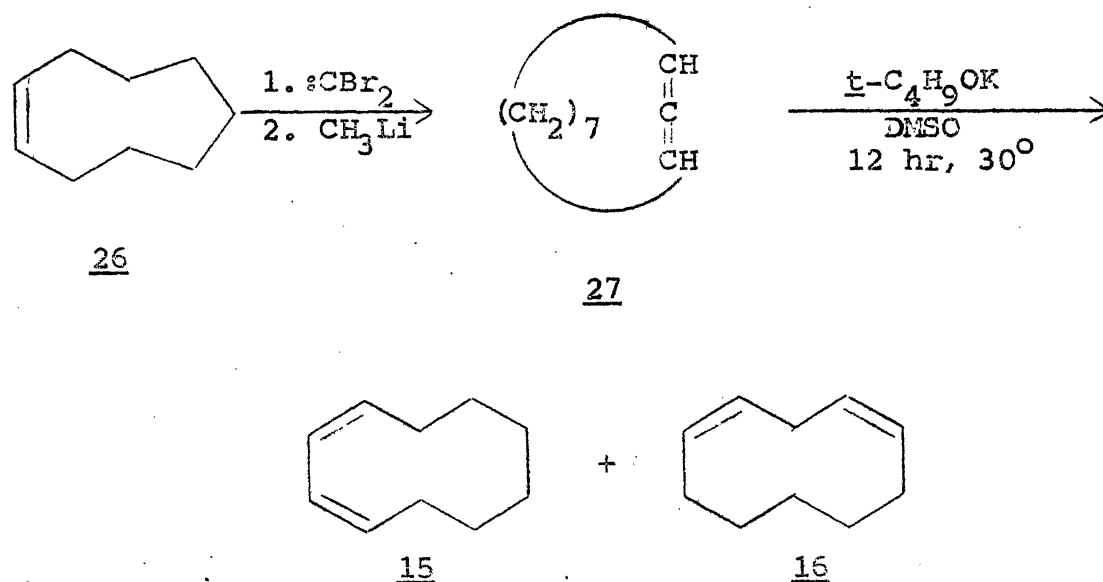
All the dienes used in the present investigation were hydroborated using borane solution in dry tetrahydrofuran.[69] The diene in dry tetrahydrofuran was added to the borane solution at 0-5° in a 1:1 molar ratio. The resulting organoborane(s) was oxidized with alkaline hydrogen peroxide. Ether was used to extract the products formed. The crude product obtained after removal

of the solvent was analysed by TLC or GLC. Pure compounds were •
obtained by column chromatography, and characterized by elemental
analysis, IR, NMR and preparation of suitable derivatives. Wher-
ever possible mixed melting points using authentic samples were
determined. The authentic samples were synthesised by un-
equivocal methods. In some cases the structural assignment of
the new compound(s) was based on the formation of a common
product from two isomeric dienes. For example, the common
product formed from the hydroboration of cis,cis-1,3-cyclonona-
diene (12), cis,cis-1,4-cyclononadiene (13) and cis,cis-1,5-
cyclononadiene (14) was characterized as cis-1,4-cyclononane
diol (35). This assignment was further substantiated by the
isomerization experiments. Hydroboration-isomerization-oxida-
tion of these dienes (12, 13 and 14) gave cis-1,5-cyclononane
diol (36) as the sole product. Moreover, the isomerization
experiments gave an idea about the nature of the intermediate
bicyclic organoborane(s) formed from the hydroboration of
dienes.[53]

I.3.1 Hydroboration of Cyclooctadienes

Hydroboration-oxidation of cis,cis-1,3-cyclooctadiene
(10) gave cis-1,3- (28) and cis-1,4-cyclooctane diols (29) in
the ratio 1:4. Isomerization of the intermediate organoboranes
from hydroboration of cis,cis-1,3-cyclooctadiene (10) followed
by oxidation gave only cis-1,5-cyclooctane diol (30) (Scheme 27).
The identity of all the products was confirmed by comparison
of the mp of the diols and their bis-p-nitrobenzoates with those

reported in the literature or by mixed mp of the diols and the bis-p-nitrobenzoates using authentic samples. Samples of cis-1,4- (29) and cis-1,5-cyclooctane diols (30) were synthesized from hydroboration of cis,cis-1,5-cyclooctadiene (11)[53] (Scheme 27).

Scheme 27

1:4
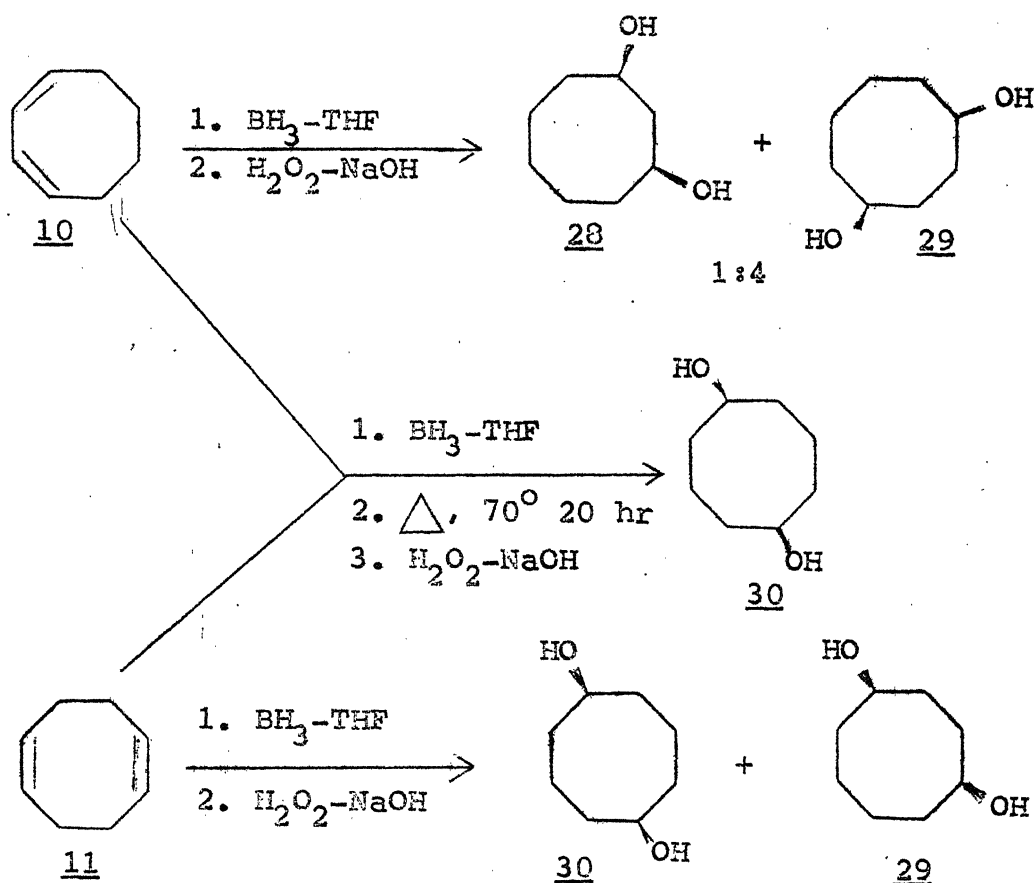
Our results clearly point out that unlike the cyclopentadiene or 1,3-cyclohexadiene,[37,41] the conjugated medium-ring diene, cis,cis-1,3-cyclooctadiene (10) is capable of undergoing cyclic hydroboration with borane in tetrahydrofuran. The formation of 28 and 29 can be explained via the bicyclic organo-

borane intermediates, 9-borabicyclo(5.1.1)nonane (31) and

9-borabocyclo(4.2.1)nonane (32). The isomerization experiment

indicates that the organoboranes (31 and 32) undergo facile

conversion to thermodynamically more stable bicyclic organo-

borane, 9-borabicyclo(3.3.1)nonane (33)(Scheme 28).

Scheme 28
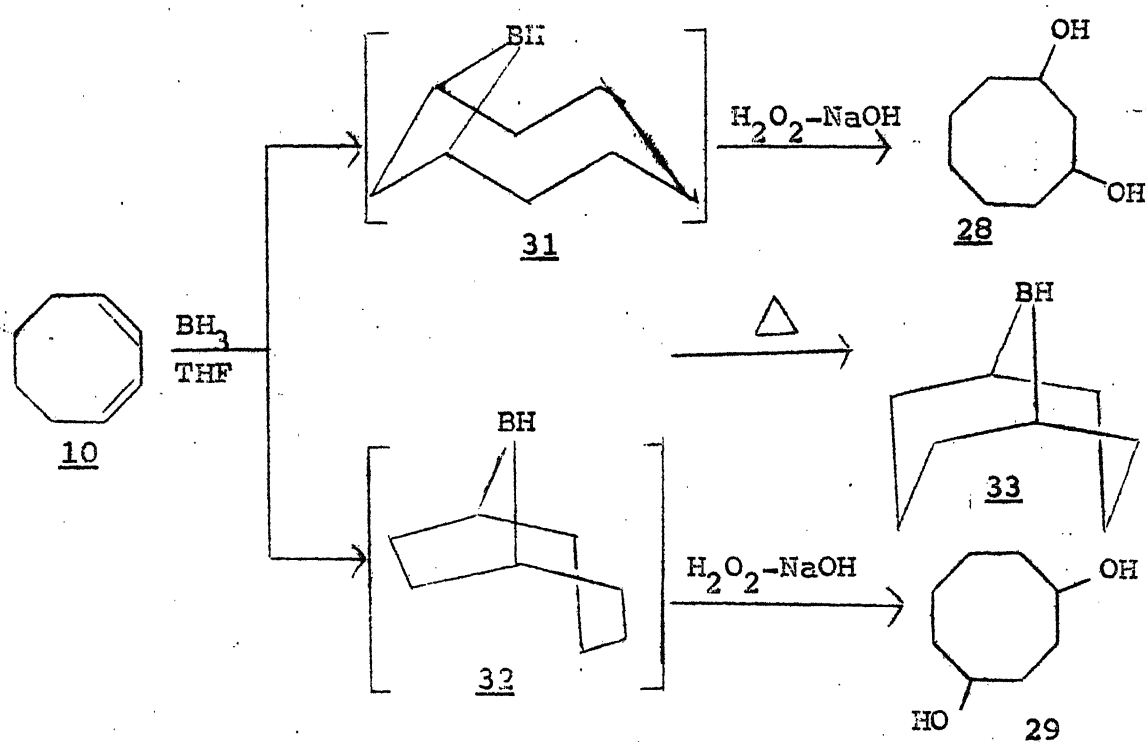
I.3.2 Hydroboration of Cyclononadienes

cis,cis-1,3-Cyclononadiene (12) on hydroboration and

oxidation provided cis-1,3- (34) and cis-1,4-cyclononane diols

(35) in the ratio 13:67. A mixture of cis-1,3- (34), cis-1,4-

(35) and cis-1,5-cyclononane diols (36) containing major amount

of 36 was obtained by hydroboration and oxidation of cis,cis-1,4-

cyclononadiene (13). Under similar conditions cis,cis-1,5-cyclo-

nonadiene (14) yielded cis-1,4- (35) and cis-1,5-cyclononane

diols (<u>36</u>) in the ratio 1:4. The hydroboration-isomerization-oxidation of <u>12</u>, <u>13</u> and <u>14</u> gave cis-1,5-cyclononane diol (<u>36</u>) as the sole product (Scheme 29).

<u>Scheme 29</u>

1. BH$_3$-THF
2. H$_2$O$_2$-NaOH

<u>12</u>   OH   OH   +   13:67   <u>35</u>

HO   <u>34</u>   OH

1. BH$_3$-THF
2. H$_2$O$_2$-NaOH

<u>13</u>   OH   OH   OH   +   OH

OH   <u>34</u>   <u>35</u>   <u>36</u>

OH (major)

1. BH$_3$-THF
2. H$_2$O$_2$-NaOH

<u>14</u>   OH   +   1:4   OH

OH   <u>35</u>   OH   <u>36</u>

<u>12</u> or <u>13</u> or <u>14</u>

1. BH$_3$-THF

2. △ , 70°, 4hr

3. H$_2$O$_2$-NaOH

OH   <u>36</u>   OH
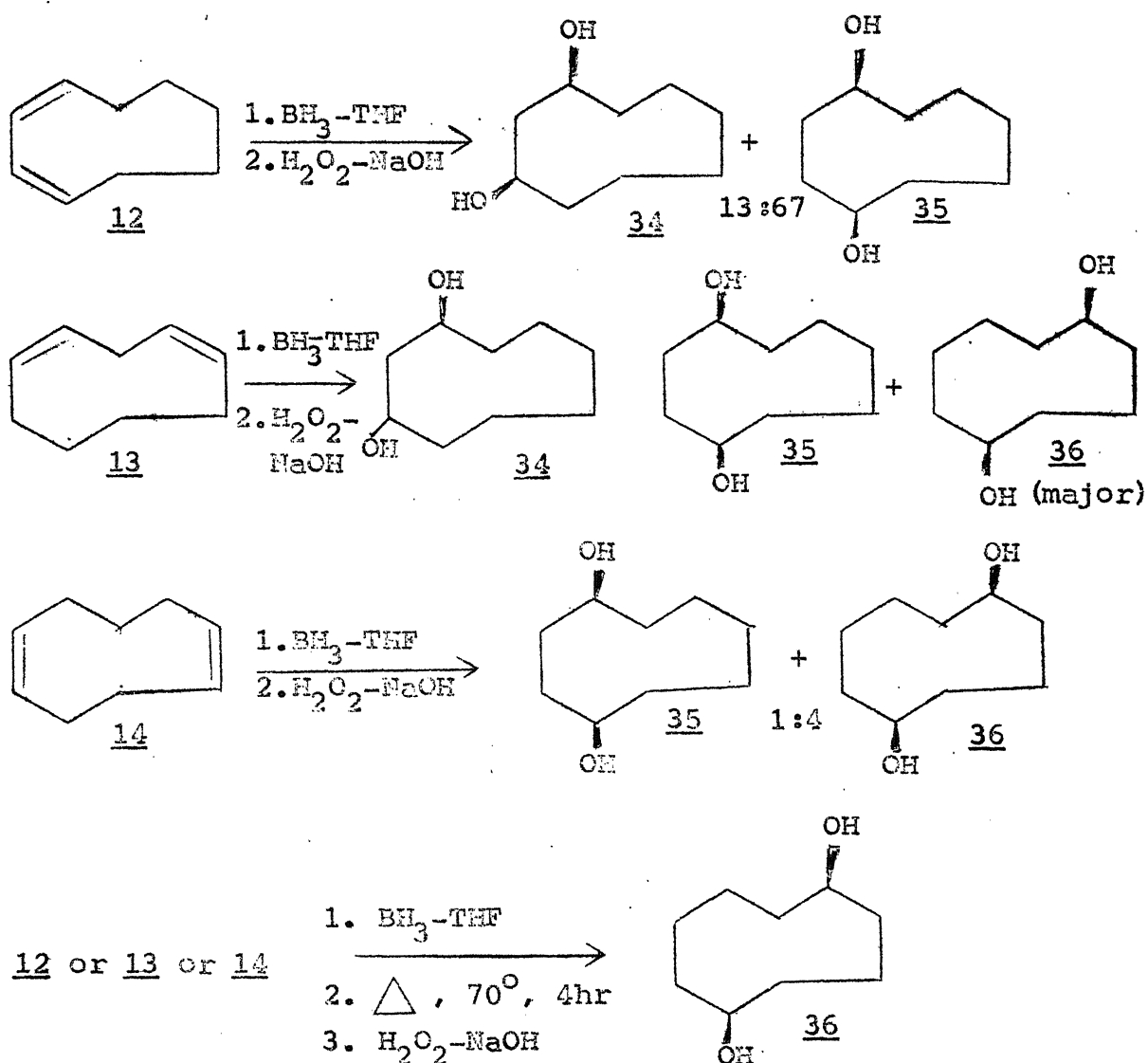
The assignment of the structures of <u>34</u> and <u>36</u> is based on the use of authentic samples prepared by unequivocal methods. cis-1,3-Cyclononane diol (<u>34</u>) was obtained as the major product

from hydroboration-oxidation of 3-hydroxycyclononene[31] (37),
whereas cis-1,5-cyclononane diol (36) was synthesized starting
from 1,2,6-cyclononatriene (25) (Scheme 30).[70] 1,2,6-Cyclo-
nonatriene (25) was hydroborated to get cis-5-cyclononen-1-one[70]
(38), which was reduced with lithium aluminium hydride to give
cis-5-cyclononen-1-ol (39). The hydroboration-oxidation of the
unsaturated alcohol provided cis-1,5-cyclononane diol (36) as
the major product.

Scheme 30
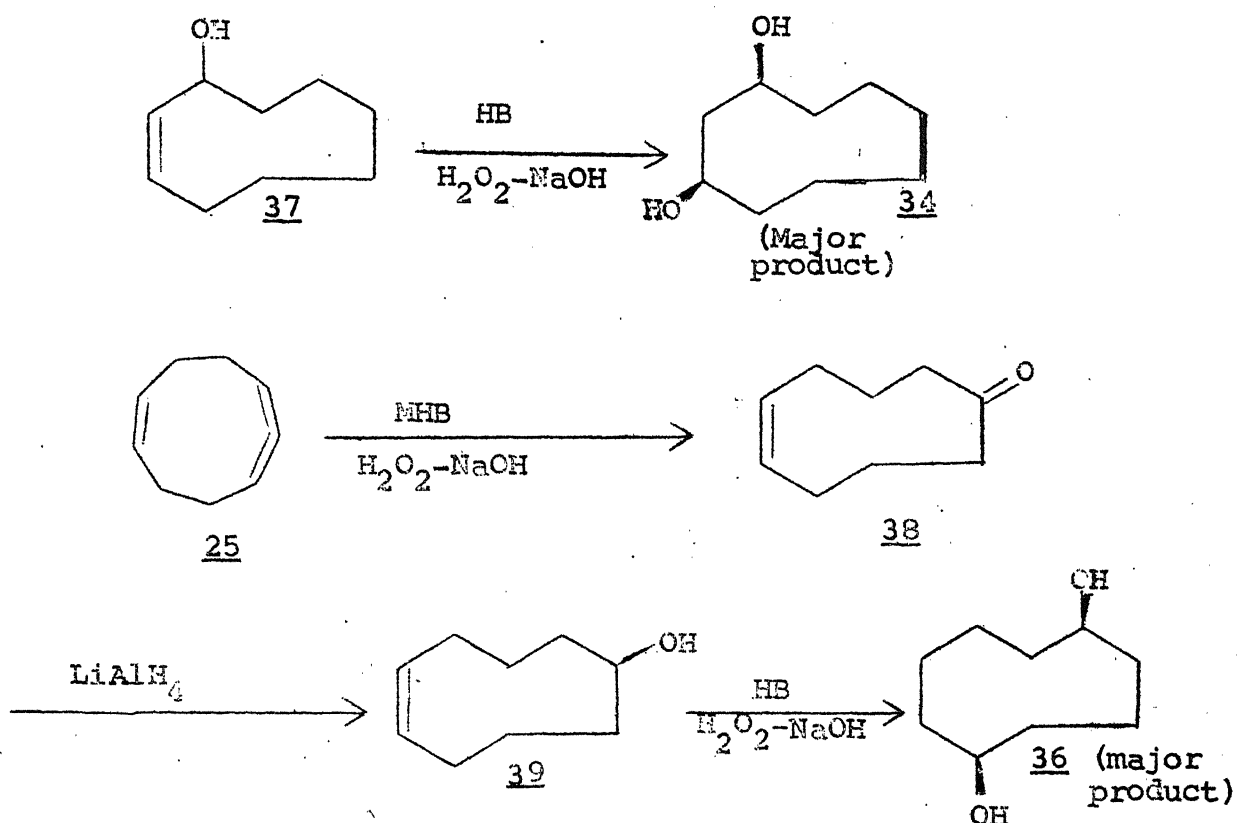
On the basis of the formation of the common diol (35)
in the hydroboration-oxidation of 12, 13 and 14, we have
assigned the diol 35 to be the cis-1,4-cyclononane diol.

Our observations on the cyclic hydroboration of isomeric cyclo-
nonadienes (12, 13 & 14) suggest that a nine-membered cyclic
diene behaves very similar to an eight-membered cyclic
diene. The results can be explained via 10-borabicyclodecanes
(40, 41 and 42) as intermediates in accordance with Brown's
postulation,[53] (Scheme 31). On the basis of thermodynamic
consideration these results show that six- and seven-membered
rings fused to a six-membered ring are the most stable boron

Scheme 31

40

+

41

Δ

42
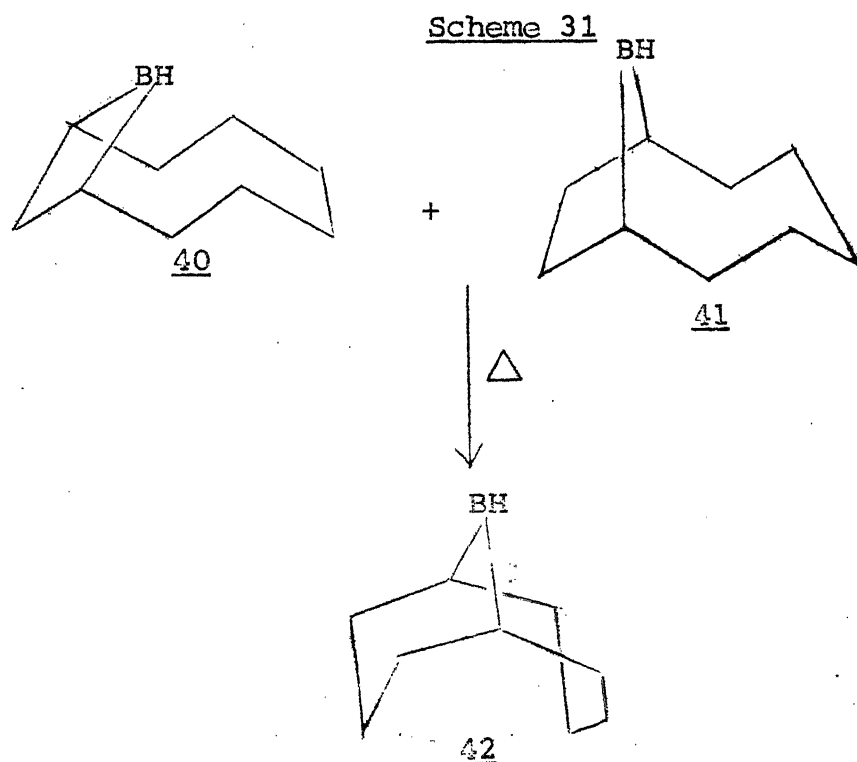
bridged bicyclic organoboranes. Furthermore, this demonstrates
the preference for six-membered boron heterocyclic rings in
isomerization reactions, which is in agreement with Saegebarth's
proposal.[40] Moreover, the fact that a fused six-membered boron
heterocycle is more stable than a five-membered one, which

in turn is more stable than a four-membered heterocycle in
eight- and nine-membered rings is acceptable based on the distri-
bution of the diols obtained from isomeric cyclooctadienes and
cyclononadienes.

In an earlier report, Prelog and coworkers[71] had obtained
the two isomeric 1,5-cyclononane diols (A and B) from cyclono-
nene epoxide. Diol A and its bis-p-nitrobenzoate were reported
to have mp 82-84° and 182° respectively. The diol (36) and its
bis-p-nitrobenzoate obtained from hydroboration-isomerization-
oxidation of cis,cis-1,5-cyclononadiene (14) had mp 70° and
182° respectively. However, the mixed mp of the two samples
of bis-p-nitrobenzoate was found to be 182°. In a private
communication Professor V. Prelog suggested that the diol
obtained from 14 is a polymorphic modification of his diol A.
Thus we assign cis-configuration to Prelog's diol A and trans-
configuration to diol B based on our findings.

I.3.3 Hydroboration of Cyclodecadienes

The results obtained from hydroboration-oxidation of
cis,cis-1,3-cyclodecadiene (15) were different from eight- and
nine-membered cyclic 1,3-dienes. The major product isolated was
characterized as trans,cis-β-decalol (45) by comparison of
of the mp of 45 and its p-nitrobenzoate reported in the
literature.[87] Furthermore, oxidation of 45 with CrO_3-pyridine
provided trans-β-decalone (46)[88] as its semicarbazone mp and
one reported in the literature are identical. Besides 45,

two more isomeric diols were obtained in small amounts, and these have not been characterized. The organoboranes formed from **15** were found to be quite stable to thermal condition. There was no change in product distribution on isomerization-oxidation of the organoboranes. In our opinion, one of the reasonable pathways[72] for the formation of the bicyclic alcohol (**45**) is _via_ _trans_-1,4-diborocyclodecane[41] (**43**) as shown in the Scheme 32. If such a proposal holds good, it should be possible to measure the amount of hydrogen liberated during oxidation procedure.

Scheme 32
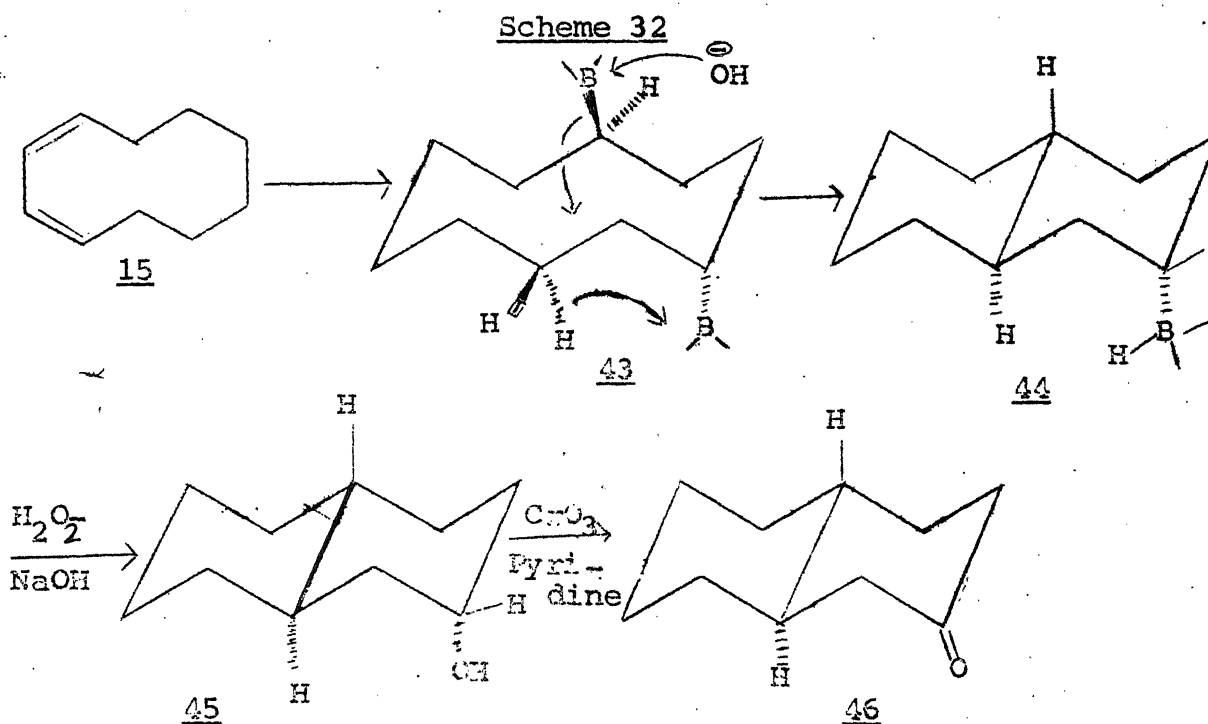
Hydroboration of _cis_,_cis_-1,6-cyclodecadiene (**18**) followed by oxidation afforded _cis_-1,5-cyclodecane diol (**47**) as the only product. The structure of the diol (**47**) is based on our results on the hydroboration-oxidation of _cis_,_cis_-1,4- (**16**) and _cis_,_trans_-1,5-cyclodecadiene (**17**) and also on the fact that both

cis- and trans-1,6-cyclodecane diols are reported in the
literature.[73] Our plan to synthesize cis-1,5-cyclodecane
diol (47) starting from octahydroazulene could not be carried
out as this tetrasubstituted olefin is known to behave in an
unusual manner with ozone.[74] The intermediate organoborane
was found to be quite stable to isomerization conditions as
the diol obtained from hydroboration-isomerization-oxidation
was found to be the same cis-1,5-cyclodecane diol (47) (Scheme 33).

Scheme 33
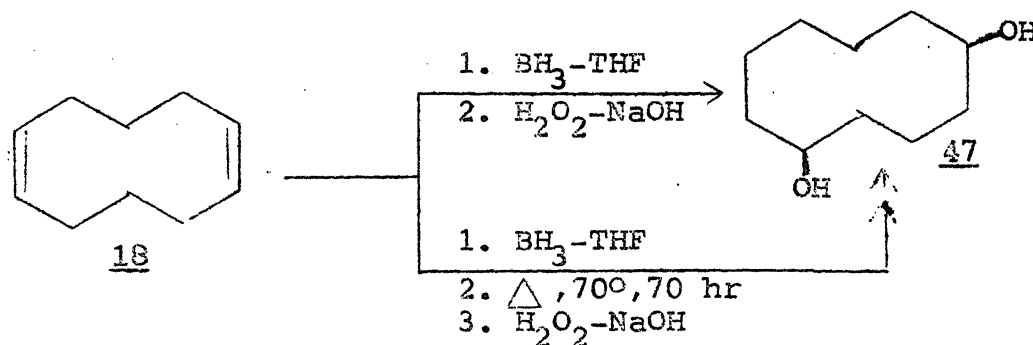
The formation of a single product (47) from 18 suggests that the
nature of the intermediate organoborane is bicyclic. An inspec-
tion of the mechanism for the formation of 11-borabicyclo(5.3.1)-
undecane (49) from 18 would reveal that in principle 18 can give
both 11-borabicyclo(5.3.1)undecane (49) and 11-borabicyclo(4.4.1)-
undecane (50) (Scheme 34). The structure 49, leading to the
formation of cis-1,5-cyclodecane diol (47) has a six-membered
boron heterocycle fused to an eight-membered ring, whereas 50

has two seven-membered rings fused together. Oxidation of 50
would lead to the formation of cis-1,6-cyclodecane diol. The
fact that no cis-1,6-cyclodecane diol was obtained from the
reaction rules out the possibility of 50 as an intermediate or
indicates that the organoborane (50) undergoes fast isomeriza-
tion to the organoborane (49) under the experimental conditions.
Further, the compatibility of 49 is possibly directed by its
thermodynamic stability.

<p style="text-align:center"><u>Scheme 34</u></p>
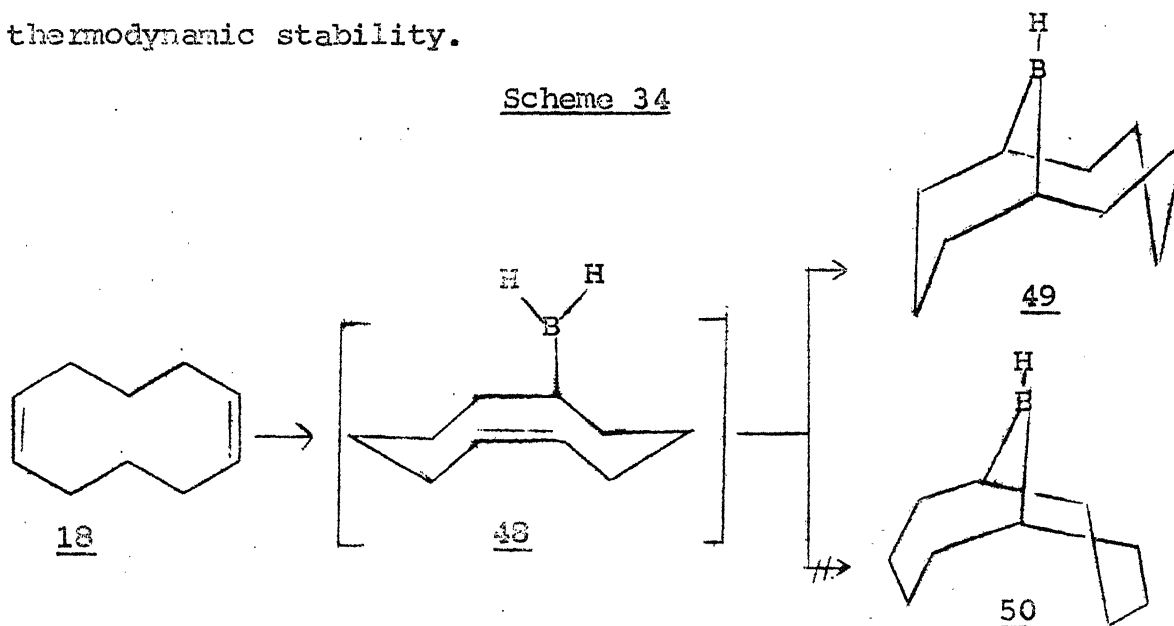
cis,cis-1,4-Cyclodecadiene (16) on hydroboration-oxidation gave
a mixture of cis-1,4-cyclodecane diol (52) and cis-1,5-cyclodecane
diol (47), latter being the major product (Scheme 35). cis-1,4-
Cyclodecane diol (52) was found to be the common product from
16 and 17, while 16 and 18 gave cis-1,5-cyclodecane diol (47)
as the common product. The formation of 52 and 47 is readily
explicable via the bicyclic organoboranes (51 and 49). It is
interesting to note that no cis-1,3-cyclodecane diol was formed
during the hydroboration-oxidation of 16 unlike the 1,4-cyclo-
nonadiene (13). No isomerization study was done with the

Scheme 35
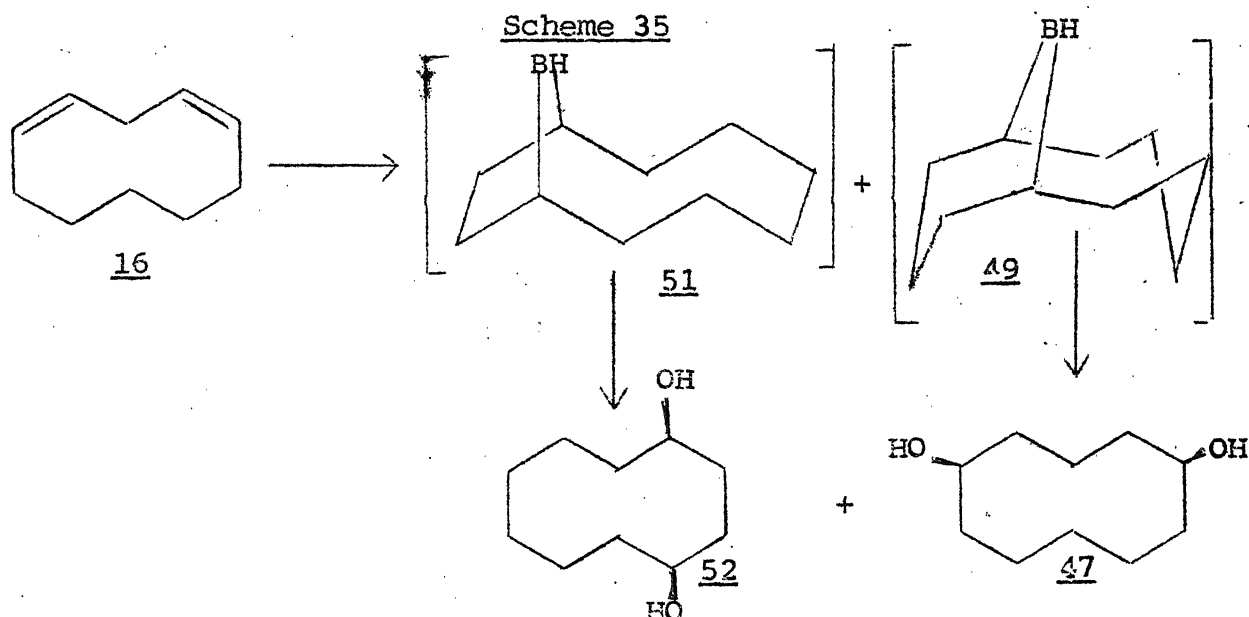
organoborane intermediates obtained from 16 as this diene (16) was difficult to synthesize.

The examination of the hydroboration of cis,trans-1,5-cyclodecadiene (17) was undertaken to study the effect of change in configuration of the double bond. Hydroboration-oxidation of 17 afforded a 6:1 mixture of cis-1,4- (52) and cis-1,5-cyclodecane diol (47) along with small amounts of cyclodecanone (53) and cyclodecanol (54). However, the isomerization of the intermediate organoboranes followed by oxidation gave mainly 1:1 mixture of cyclodecanone (53) and cyclodecanol (54) to our surprise (Scheme 36). No attempt was made to look for the possible isomeric cyclodecane diols in the residue left after distillation of cyclodecanone (53) and cyclodecanol (54).

It has been shown that monohydroboration-protonolysis[75] of cis,trans-1,5-cyclodecadiene (17) gives cis-cyclodecene. This shows that the highly reactive trans double bond adds to

Scheme 36
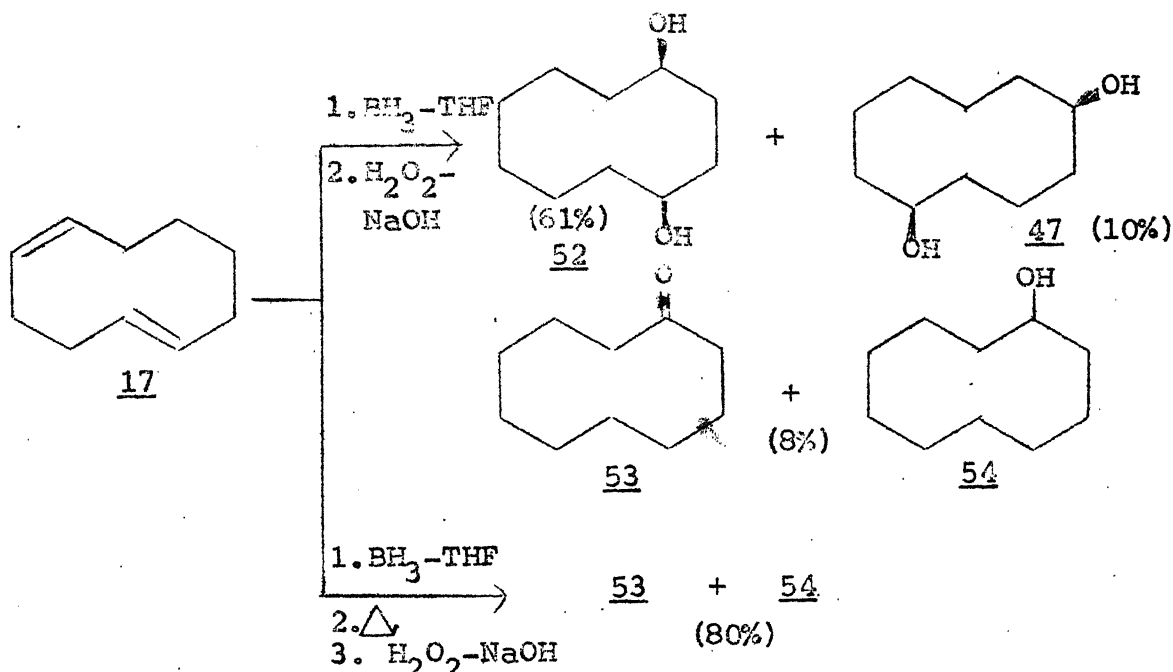
B-H bond in preference to the cis-double bond. Examination of the intermediate organoboranes (55 and 48) after monohydrobora- tion reveals that the subsequent addition of B-H to the cis- double bond can lead to the formation of three possible isomeric 11-borabicycloundecanes (49 50 and 51) (Scheme 37). Since cis-1,4-cyclodecane diol (52) is formed as the major product during hydroboration-oxidation of 17, we emphasize that the initial boron attack is probably controlled by the conformation of the diene to give 55 as the major product. The predominance of 51 over 49 from 55 seems to arise from a kinetically controlled process dictated by the conformation of 55.

The isomerization-oxidation of the intermediate organo- boranes from cis,trans-1,5-cyclodecadiene (17) clearly points

Scheme 37
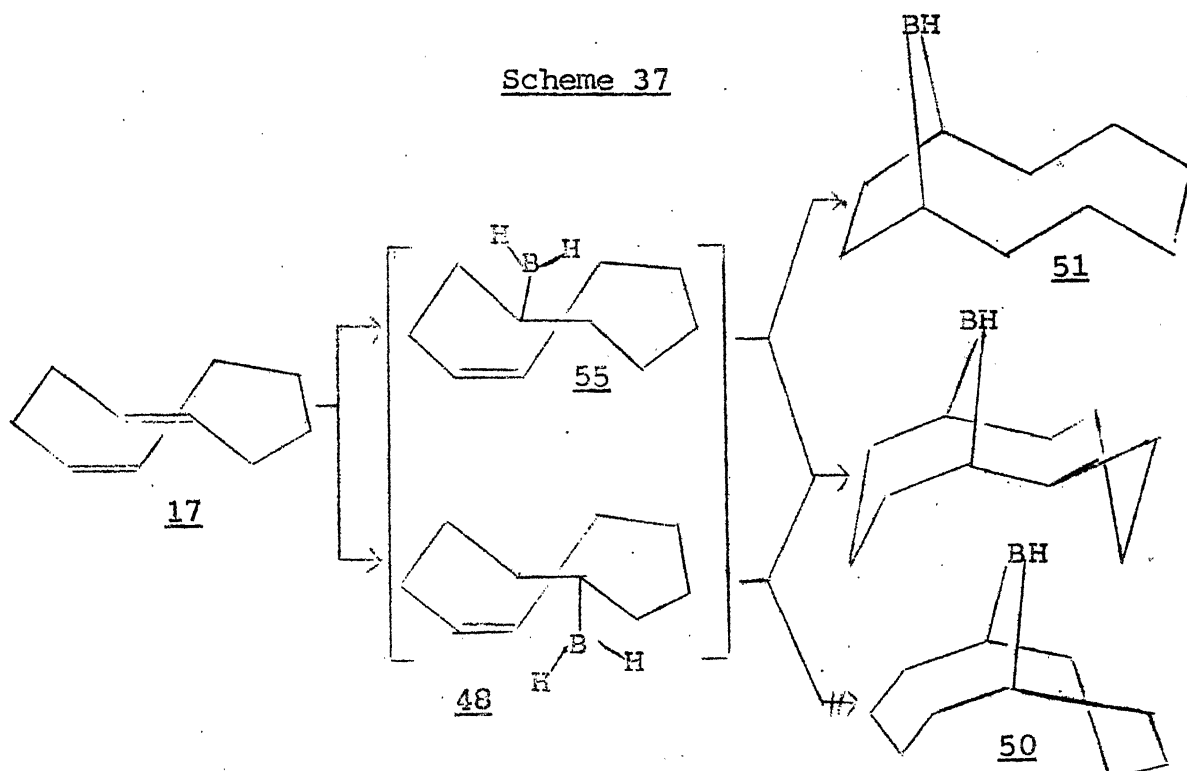
out the instability of 51. A rationale for this can be

offered in terms of isomerization of 51 to vinyl organoborane

(56) which can give rise to cyclodecanone (53) as well as cyclo-

decanol (54) (Scheme 38). The vinyl organoborane (56) can arise

from 51 either by several elimination-addition steps or in a

single step as shown in the Scheme 38. Vinyl organoborane (56)

once formed can act as a hydroborating agent giving rise to a

gem-diboro compound (57) and/or vicinal-diboro compound (58).

Hydrolysis of gem- or vicinal-diboro compound followed by oxida-

tion is known to give monoalcohol.[76]

In summary, these reactions provide a convenient stereo-

specific synthesis of many isomeric cis-cyclic diols in eight-,

nine- and ten-membered rings which are otherwise difficult

to prepare. The isomerization experiments with organoboranes

Scheme 38
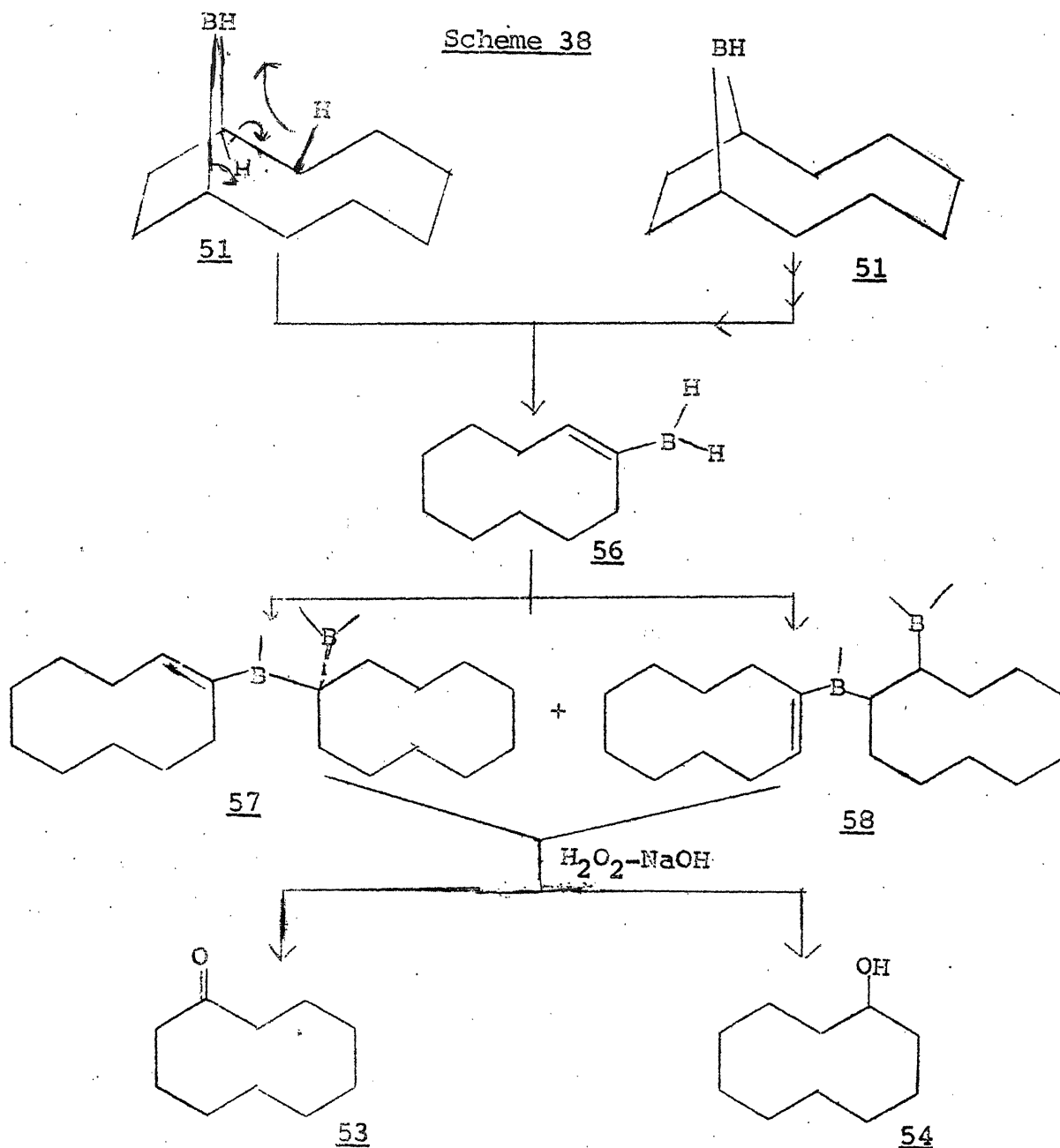
from eight- and nine-membered isomeric dienes reveal the relative thermodynamic stability of the various possible bicyclic organoboranes. Our results with ten-membered isomeric cyclic dienes point out the diversity in the cyclic hydroboration reaction in the same medium-ring. The hydroboration of cis,cis-1,3-cyclodecadine (15) can be used in the synthesis of trans,cis-β-decalol (45)

in one step. The hydroboration of cis,trans-1,5-cyclodecadiene

(17) seems to be interesting from mechanistic point of view. It

brings forth the configurational and conformational effects in

hydroboration and isomerization studies.

I.4 EXPERIMENTAL

Boiling points are uncorrected. Melting points were taken

in open capillaries using Thomas-Hoover capillary melting point

apparatus and are uncorrected. Infrared (IR) spectra were

recorded on a Perkin-Elmer Model 521 using potassium bromide

discs or as liquid film between sodium chloride plates. Nuclear

magnetic resonance (NMR) spectra were obtained with a Varian

Associates A-60 NMR spectrometer in deuterated chloroform with

tetramethylsilane as the internal standard. Gas liquid chroma-

tographic (GLC) analyses were done with Aerograph Model 90-P

instrument. The following liquid phases were employed for the

preparation of chromatographic columns (percentage by weight

on 60/80 mesh chromosorb-P): 15% silicone rubber, 20% carbowax-

20M, 15% carbowax-20M 5% silver nitrate and 20% propylene gly-

col,5% silver nitrate (F & M Scientific Corporation Avondale,

Pennsylvania, U.S.A.). Silica gel (ASW) or basic alumina

(E. Merck) was used for thin layer chromatography (TLC). Column

chromatography was done on basic alumina, columns being prepared

from its slurry in petroleum ether (60-80°). Microanalyses were

done by Mr. A.H. Siddiqui of the Department of Chemistry, Indian

Institute of Technology, Kanpur, India.

Starting Materials

cis,cis-1,5-Cyclooctadiene (Aldrich Co.), cis,cis-1,3-cyclooctadiene (Columbia), cis-cyclooctene (Columbia), cis,trans-1,5-cyclodecadiene (Cities Service Co.), cis,cis-1,6-cyclodecadiene (Cities Service Co.), bromoform (E. Merck), methyl iodide (E. Merck), lithium (E. Merck), potassium (Fischer), sodium borohydride (Metal Hydride Inc.) and hydrogen bromide solution (BDH) were used. Diglyme (Ansul Co.) was kept over calcium hydride for 24 hr, decanted and distilled over slight excess of lithium aluminium hydride under reduced pressure (bp 63-64° at 15 mm). Boron trifluoride ethyl etherate (Eastman) was treated with a small quantity of dry ether so as to ensure an excess of this component and distilled under reduced pressure over calcium hydride (bp 46-47° at 10 mm). Tetrahydrofuran (BDH) was refluxed over sodium, decanted and distilled over lithium aluminium hydride. t-Butanol (BDH) was refluxed over metallic sodium for about 5 hr and the fraction boiling at 79-80° was collected. Dimethyl sulphoxide (BDH) was kept over potassium hydroxide for several hr and distilled over calcium hydride at 85° at 12 mm.

General Method of Synthesis of 1,1-Dibromocyclopropane Derivative[60]

In a 1 l three-necked flask fitted with an efficient mechanical stirrer, a condenser, and nitrogen gas inlet and outlet was placed dry t-butanol (500 ml). Potassium (20.0 g, 0.50 g atom) was cut into small pieces and added slowly to t-butanol in nitrogen atmosphere and the contents of the flask

were stirred. After, all the potassium dissolved at room-temperature, the excess t-butanol was distilled off. The last traces of t-butanol were removed using a vacuum pump for a period of 2 hr. The solid was crushed into a nice powder and dry petroleum ether (40-60°) was added. The flask was cooled to -10° and the olefin (0.50 mol) was added. Bromoform (0.50 mol) was then added dropwise over a period of 6 hr to the well cooled flask with stirring. When the addition was over, stirring was continued for one hr. Water was added to destroy the unreacted base and the bromo compound was extracted with petroleum ether (40-60°) and dried over anhydrous magnesium sulphate. The solvent, the unreacted bromoform and the olefin were removed by distillation under vacuum. Finally, the dibromo compound was distilled under reduced pressure.

Preparation of Methyllithium[77]

A 1 l two-necked flask fitted with an efficient water condenser, a dropping funnel and nitrogen gas inlet and outlet, was mounted on a magnetic stirrer. Lithium (7.0 g, 1 g atom) and dry ether (200 ml) were placed in the flask which was swept with dry nitrogen. Methyl iodide (71 g, 0.50 mol) was diluted with 200 ml of dry ether and a few ml was allowed to drop into the flask. As soon as the reaction started (noted by the gentle reflux of ether), rest of the methyl iodide solution was added at such a rate that ether refluxed slowly. After the completion of addition, stirring was continued for another hr.

General Method of Synthesis of Allenes[61]

The 1,1-dibromocyclopropane derivative (0.25 mol) in 200 ml of dry ether was placed in a 1 1 three-necked flask fitted with a dropping funnel and a mechanical stirrer. The flask was swept with a stream of dry nitrogen and cooled to -50 to -60° using ethanol and liquid nitrogen as the coolant. Methyllithium prepared as above was filtered through glasswool in a current of dry nitrogen into a separatory funnel and added dropwise into the flask with stirring over a period of one hr. After an additional hr of stirring, the flask was allowed to come to ambient temperature, and water was added slowly to destroy excess methyllithium. The organic compound was extracted with ether, washed with water several times, and kept over anhydrous magnesium sulphate. Ether was removed and the allene was distilled under reduced pressure.

Preparation of 9,9-Dibromobicyclo(6.1.0)nonane

Potassium t-butoxide was prepared from potassium (20 g, 0.50 g atom) and dry t-butanol (600 ml). After the removal of excess of t-butanol, dry petroleum ether (500 ml) and cis-cyclo-octene (66 g, 0.60 mol) were added followed by slow addition of bromoform (126 g, 0.50 mol) at 0°. Usual extraction procedure afforded 100 g (74%) of 9,9-dibromobicyclo(6.1.0)nonane, bp 85-86° (0.2 mm), n_D^{25} 1.5519 (lit[61] bp 80-82° at 0.1 mm, n_D^{20} 1.5520). The compound was saturated to bromine and neutral potassium permanganate. GLC analysis of the sample on a 2 ft silicone rubber column indicated it to be single.

Preparation of 1,2-Cyclononadiene

From 9,9-dibromobicyclo(6.1.0)nonane (56.4 g, 0.20 mol) and methyllithium from lithium (5.6 g, 0.80 g atom) and methyl iodide (56.8 g, 0.40 mol) was obtained 20.7 g (85%) of 1,2-cyclononadiene, bp 63° at 17 mm, n_D^{25} 1.5054 (lit[78] bp 62° at 16 mm, n_D^{20} 1.5060).

IR spectrum of the allene showed band at 1950 cm^{-1}, characteristic of the allenic group. GLC analysis on a 10 ft carbowax column showed it to be one component. NMR showed allenic protons at δ 5.17 (2 protons) as a complex multiplet.

Preparation of 3-Bromocyclononene

Hydrogen bromide solution in acetic acid (12 ml, 45% w/v solution) was added dropwise with stirring at 10-15° to 1,2-cyclononadiene (7.32 g, 0.06 mol). After the addition was over stirring was continued for about two hr. The mixture was poured into about 200 ml of water, neutralized with sodium bicarbonate, extracted with petroleum ether (40-60°) and the crude product was subjected to molecular distillation to obtain 10.3 g (85%) of 3-bromocyclononene, bp 76° at 4 mm, n_D^{34} 1.5167. It behaved like an allylic bromo compound since it gave an immediate precipitate with silver nitrate in aqueous methanol solution. A careful GLC analysis on a 2 ft silicone rubber column indicated it to be pure. The IR spectrum had absorptions at 2018, 1635 and 710 cm^{-1}. There was no IR absorption in the 960 cm^{-1} region suggesting the cis configuration as the most likely for the double bond. The NMR spectrum in carbon tetrachloride showed multiplets

at δ 5.6 (m, 2H),olefinic protons, 5.00 (m, 1H), methine, and 2.40 - 1.00 (m, 12H),methylene protons. The identity was further confirmed by comparison of GLC, IR and NMR with that of an authentic sample.[79]

Preparation of cis,cis-1,3-Cyclononadiene[62]

Sublimed potassium t-butoxide (2.2 g, 0.02 mol) was dissolved in dry DMSO (16 ml) in a 50 ml two-necked flask fitted with a condenser, an inlet and an outlet for dry nitrogen gas. 3-Bromocyclononene (4 g, 0.02 mol) was added in one portion and the contents of the flask were stirred for 5 min. The reaction mixture was poured into water, extracted with petroleum ether, washed thoroughly with water and dried over anhydrous magnesium sulphate. Distillation of the crude product afforded 1.72 g (72%) of cis,cis-1,3-cyclononadiene,bp 80° at 30 mm. The product corresponded in all respects (GLC, IR and NMR with an authentic sample.[63]

Preparation of 9,9-Dibromobicyclo(6.1.0)non-2-ene

Following the general procedure described previously, from cis,cis-1,3-cyclooctadiene (135 g, 1.25 mol), potassium (10 g, 0.25 g atom), 300 ml of dry t-butanol and bromoform (69.5 g, 0.27 mol) at 0° was obtained 50 g (71%) of 9,9-dibromobicyclo(6.1.0)non-2-ene, bp 70-72° at 0.1 mm, n_D^{24} 1.5678 (lit.[80] bp 74-75° at 0.15 mm, n_D^{24} 1.5678). GLC analysis of the product on a 2 ft silicone rubber column indicated it to be pure.

Anal. for $C_9H_{12}Br_2$: Calcd: C, 38.60; H, 4.32.

Found: C, 38.42; H, 4.20.

Preparation of Bicyclo(6.1.0)non-2-ene

A 1 1 three-necked flask was equipped with a mercury
sealed mechanical stirrer, a dry-ice condenser leading to a
mercury trap and an inlet for ammonia gas. A slow stream of
ammonia was swept through in the beginning followed by freezing
the ethyl acetate in the condenser using liquid nitrogen. About
600 ml of ammonia was condensed in the flask directly from the
tank. After the collection was over, the gas inlet was replaced
by a stopper. Freshly cut sodium (9.2 g, 0.4 g atom) was added
to liquid ammonia and allowed to stir for 30 min. 9,9-Dibromo-
bicyclo(6.1.0)non-2-ene (28 g, 0.1 mol) in 100 ml of ether was
added by means of a dropping funnel directly into the flask.
Stirring was continued for 6 hr to ensure completion of reduction.
Solid ammonium chloride was added until the solution became
colourless, and ammonia was allowed to evaporate. The residue
was diluted with water and extracted with ether thrice. The
combined extracts were washed with dilute hydrochloric acid
followed by water until it became neutral. The solution was
dried over anhydrous magnesium sulphate and the solvent was
removed at reduced pressure. The residue was fractionated to
obtain 5.5 g (37%) of bicyclo(6.1.0)non-2-ene, bp 80° at 20 mm
(lit.[80] bp 50-52° at 0.1 mm). GLC analysis indicated it to be
a single substance. Its NMR spectrum exhibited
signals at δ5.2-5.8 (m, 2H) olefinic protons, 0.5-2.7 (m,11H)

methylene protons and -0.1 to -0.3 (m, 1H) allylic cyclopropyl proton.

Preparation of cis,cis-1,4-Cyclononadiene[64]

Pyrolysis of bicyclo(6.1.0)non-2-ene (3.6 g, 0.03 mol) in nitrogen atmosphere at a bath temperature of 180-185° for 10 hr provided 2.4 g (66%) yield of cis,cis-1,4-cyclononadiene after molecular distillation. The purity of the diene was checked by GLC. IR and NMR data were in agreement with the data reported in the literature.[64] The IR spectrum had strong absorption at 720 cm^{-1} characteristic of a cis double bond and no absorption at 980 cm^{-1} characteristic of a trans double bond. NMR spectrum showed lines at δ 5.47 (m, 4H) vinylic protons, 2.78 (m, 2H) bisallylic protons, 2.18 (m, 4H) allylic protons and 1.51 (m, 4H) ring methylene protons.

Preparation of 1,2,6-Cyclononatriene

In a 1 1 three-necked flask fitted with a mechanical stirrer, a dropping funnel, an inlet and an outlet for dry nitrogen gas, was placed cis,cis-1,5-cyclooctadiene (54.0 g, 0.5 mol) and 40.0 g of carbon tetrabromide (0.12 mol) in 200 ml of dry ether and cooled to -65°. To the stirred mixture of this, was added methyllithium (0.125 mol) in 100 ml of dry ether over a period of 45 min. The stirring was continued at -65° for 30 more min, then methyllithium (0.135 mol) in ether was added over a period of 45 min. The reaction mixture was further stirred for 30 min and water was added. The ethereal

layer was separated, washed with water until neutral and dried over anhydrous magnesium sulphate. Ether was removed and the allene was fractionated to obtain 9.4 g (62%) of 1,2,6-cyclo-nonatriene, bp 61° at 13 mm, n_D^{25} 1.5212 (lit.[61] bp 61 at 13 mm, n_D^{24} 1.5216). The identity was established by comparison of GLC retention times and IR spectra with that of an authentic sample.

Preparation of cis,cis-1,5-Cyclononadiene

Following the procedure described for the preparation of cis-cyclononene, from 1,2,6-cyclononatriene (12 g, 0.10 mol), sodium (9.2 g, 0.40 g atom) and 250 ml of liquid ammonia, was obtained 10 g (83%) of cis,cis-1,5-cyclononadiene, bp 64° at 20 mm, n_D^{25} 1.4922 (lit.[65] bp 56° at 17 mm, n_D^{22} 1.4927). The identity was established by comparison of GLC retnention times and IR spectra with that of authentic sample.[65,66]

Preparation of cis-Cyclononene

A 1 l three-necked flask was fitted with an inlet tube for ammonia gas, a mechanical stirrer with glass paddle and a large solid ethyl acetate reflux condenser leading to a mercury bubbler. About 500 ml of liquid ammonia was collected directly from the tank without purification. Sodium (20.7 g, 0.90 g atom) was added in the form of small pieces and the resulting blue solution was stirred for 15 min. 1,2-Cyclononadiene (36.6 g, 0.30 mol) in 100 ml of anhydrous ether was added dropwise with stirring. After stirring for 1 hr following the addition, the excess sodium was destroyed by careful addition of ammonium

chloride. The product was isolated by adding water to the residue followed by extraction with ether. The ether extract was dried over anhydrous magnesium sulphate. Distillation of the crude product gave 30.5 g (83%) of cis-cyclononene, bp 81° at 40 mm, n_D^{30} 1.4740 (lit.[81] bp 167-169° at 740 mm, n_D^{20} 1.4799). The IR spectrum was identical with that of an authentic sample. GLC of the product on a 5 ft carbowax-silver nitrate column indicated it to be single.

Preparation of 10,10-Dibromobicyclo(7.1.0)decane

Following the general procedure described previously from cis-cyclononene (24.0 g, 0.2 mol), bromoform (50.6 g, 0.2 mol), potassium (8 g, 0.2 g atom) and 200 ml of dry t-butanol at -15° was obtained 40.9 g (68%) of 10,10-dibromobicyclo(7.1.0)-decane, bp 80° at 0.05 mm, n_D^{30} 1.5492 (lit.[60] bp 100° at 0.2 mm). GLC analysis of the compound on a 2 ft silicone rubber column gave a single peak.

Preparation of 1,2-Cyclodecadiene

Methyllithium prepared from lithium (2.8 g, 0.4 g atom) and methyl iodide (28.4 g, 0.2 mol) was treated with 10,10-dibromobicyclo(7.1.0)decane (29.6 g, 0.1 mol) in dry ether at -40 to -45°. The usual extraction procedure afforded 10.8 g (80%) of 1,2-cyclodecadiene, bp 60° at 4 mm, n_D^{30} 1.5060 (lit.[82] bp 74° at 10 mm, n_D^{25} 1.5071). GLC analysis on a 10 ft carbowax column showed it to be single. IR spectrum showed characteristic allene band at 1950 cm^{-1}. NMR showed a band at δ 4.90 (m, 2H) allenic protons.

Preparation of cis,cis-1,3-Cyclodecadiene[67]

Potassium t-butoxide, obtained by dissolving potassium

in t-butanol and removing excess of t-butanol, was sublimed at

170° (bath temperature) under 0.02 mm vacuum. Sublimed potassium

t-butoxide (4.48 g, 0.04 mol) was dissolved in dry dimethyl

sulphoxide (20 ml) in a 100 ml two-necked flask fitted with a

condenser, an inlet and an outlet for dry nitrogen gas. 1,2-Cyclo-

decadiene (2.72 g, 0.02 mol) was added in one portion and the

contents of the flask were stirred for 12 hr at room temperature.

The product was extracted with petroleum ether (40-60°), washed

thoroughly with water and dried over anhydrous magnesium sulphate.

The distillation of the crude product afforded 2.1 g (77%) of

reaction product, bp 81° at 18 mm. GLC analysis indicated it

to be a mixture of two products in the ratio 80:20 devoid of any

allene. The components were separated by preparative GLC and

the compounds were identified as cis,cis-1,3- and 1,4-cyclodeca-

diene respectively using   authentic samples.[68]

Preparation of Borane in Tetrahydrofuran[83]

In a 1 l three-necked flask equipped with a pressure-equa-

lizing dropping funnel, an inlet and an outlet for nitrogen gas

was placed 950 ml of a 1M solution of sodium borohydride in diglyme.

The outlet was connected to a dispersion tube dipped in 500 ml

of dry tetrahydrofuran in a 1 l two-necked flask, through a tygon

tubing. The outlet of the other flask was connected to a mercury

bubbler. Diborane, generated by the addition of 1.9 mol of boron

trifluoride etherate was passed into tetrahydrofuran. Estimation

of the borane by hydrolysis indicated its concentration to be
2.0M in THF.

General Method of Hydroboration[53]

In a 250 ml three-necked flask equipped with a water
condenser, equilibrating dropping funnel, a low temperature
thermometer, an inlet and an outlet for dry nitrogen, was placed
borane solution (15 ml, 2M BH_3-THF). The diene (0.3 mol) in
20 ml dry tetrahydrofuran was allowed to drop into the borane
solution over a period of 30 min keeping the temperature between
0 to 5°. The contents of the flask were allowed to stir for an
additional 30 min at 5 to 10° and then for 2 hr at room tempera-
ture. The organoborane obtained was oxidized as such or isomeri-
zed and then oxidized at 0° by adding 15 ml of 3M sodium hydroxide
followed by 15 ml of 30% hydrogen peroxide. Isomerization was
done by refluxing the mixture (67°) for the requisite time. The
product was extracted with ether, washed with water and dried
over anhydrous magnesium sulphate. Further separation and puri-
fication of the individual components were achieved by column
chromatography through alumina.

Hydroboration-Oxidation of cis,cis-1,3-Cyclooctadiene

Hydroboration-oxidation of cis,cis-1,3-cyclooctadiene
(3.3 g, 0.03 mol) in 20 ml dry tetrahydrofuran with 15 ml of
2M borane solution afforded 3.2 g of viscous oil. TLC analysis
on alumina plate with ethyl acetate as solvent indicated it to
be a mixture of two components. This material was dissolved in

minimum amount of benzene and chromatographed in benzene-ether on basic alumina. Elution of the column with a mixture (4:1) of benzene and ether gave 0.6 g (14%) of a gummy material, which crystallized out on trituration with petroleum-ether. The solid material was recrystallized from ethyl acetate, mp 57°. IR showed bands at 3500 and 1050 cm^{-1} for O-H and C-O stretchings respectively. Thus the product was identified as cis-1,3-cyclooctane diol. This yielded a bis-p-nitrobenzoate, mp 129° (from chloroform-methanol) comparable with that reported in the literature[84] (diol, mp 57-58°, bis-p-nitrobenzoate, mp 129°).

Anal. for $C_8H_{16}O_2$: Calcd: C, 66.60; H, 11.10.

Found: C, 66.50; H, 11.09.

for $C_{22}H_{22}O_8N_2$: Calcd: C, 59.20; H, 4.97; N, 6.33.

Found: C, 59.00; H, 5.00; N, 6.20.

Further elution of the column with ether gave 2.5 g (60%) of a solid (recrystallized from ethyl acetate) mp 84°. IR indicated it to be an alcohol identified as cis-1,4-cyclooctane diol from elemental analysis and mixed mp of the diol with an authentic sample obtained from the hydroboration of cis,cis-1,5-cyclooctadiene[53] (lit[85] diol, mp 83-84.5°; bis-p-nitrobenzoate mp and mixed mp 161-162°).

Anal. for $C_8H_{16}O_2$: Calcd: C, 66.60; H, 11.10.

Found: C, 66.30; H, 11.30.

for $C_{22}H_{22}O_8N_2$: Calcd: C, 59.20; H, 4.97; N, 6.33.

Found: C, 58.90; H, 4.80; N, 6.20.

Hydroboration-Isomerization-Oxidation of cis,cis-1,3-Cycloocta-diene

The organoborane obtained from 3.3 g (0.03 mol) of cis,cis-1,3-cyclooctadiene and 15 ml of 2M borane solution was refluxed in dry tetrahydrofuran (67°) for a period of 20 hr. It was cooled to 0° and hydrolyzed with water followed by oxidation with alkaline hydrogen peroxide. The usual work-up afforded 3.1 g (72%) of a solid which showed a single spot on silica gel coated plate and was found to be different from cis-1,3- or cis-1,4-cyclooctane diol. It was recrystallized from ethyl acetate. IR revealed it to be an alcohol only and was identified as cis-1,5-cyclooctane diol on the basis of the mixed mp of the diol and its bis-p-nitrobenzoate with those of authentic samples. The authentic sample of cis-1,5-cyclooctane diol was obtained by hydroboration-isomerization-oxidation of cis,cis-1,5-cyclooctadiene.[53] Diol mp and mixed mp 74°; bis-p-nitrobenzoate, mp and mixed mp 181-182° (lit.[86] diol mp 73.4-74.8°, bis-p-nitrobenzoate mp 181.4-182.6°).

Anal. for $C_8H_{16}O_2$: Calcd: C, 66.60; H, 11.10.

Found: C, 66.50; H, 11.09.

for $C_{22}H_{22}O_8N_2$: Calcd: C, 59.20; H, 4.97; N, 6.33.

Found: C, 59.50; H, 4.90; N, 6.20.

Hydroboration-Oxidation of cis,cis-1,5-Cyclooctadiene

Hydroboration-oxidation of cis,cis-1,5-cyclooctadiene (3.3 g, 0.03 mol) with 15 ml of 2M borane solution in tetra-

hydrofuran afforded 3.0 g of a viscous oil which was separated into cis-1,5-cyclooctane diol (72%) and cis-1,4-cyclooctane diol (28%) by column chromatography.

The isomerization-oxidation of the organoborane from cis,cis-1,5-cyclooctadiene (3.3 g, 0.03 mol) gave 3.23 g (78%) of cis-1,5-cyclooctane diol.

Hydroboration-oxidation of cis,cis-1,3-Cyclononadiene

Hydroboration-oxidation of cis,cis-1,3-cyclononadiene (1.85 g, 0.015 mol) with 7.5 ml of 2M borane solution yielded 1.9 g of viscous oil, which gave two spots on alumina plate (TLC analysis). This material was chromatographed on basic alumina using benzene-ether. Elution of the column with ether-benzene (1:9) gave 0.3 g of a thick oil (13%), IR of which showed absorptions for O-H and C-O. It failed to crystallize. Analysis of the p-nitrobenzoate derivative indicated the product to be a diol, bis-p-nitrobenzoate of which had mp 117-118°. This was identified as cis-1,3-cyclononane diol using an authentic sample prepared from hydroboration-oxidation of 3-hydroxycyclononene.[31]

Anal. for $C_{23}H_{24}N_2O_8$: Calcd: C, 60.50; H, 5.20; N, 6.14.

Found: C, 59.81; H, 5.40; N, 5.90.

Further elution of the column with ether gave 1.6 g of solid (60%), mp 82° (from ethyl acetate), bis-p-nitrobenzoate, mp 147-148° (from chloroform-methanol). IR spectrum indicated it to be an alcohol. The solid was characterized as cis-1,4-cyclo-

nonane diol based on the hydroboration-oxidation of cis,cis-1,4- and 1,5-cyclononadiene. The common diol obtained from these two dienes had mp and mixed mp 32°, bis-p-nitrobenzoate mp and mixed mp 147°.

Anal. for $C_9H_{18}O_2$: Calcd: C, 68.30; H, 11.39.

Found: C, 68.41; H, 11.16.

for $C_{23}H_{24}N_2O_8$: Calcd: C, 60.50, H, 5.20; N, 6.14.

Found: C, 60.40; H, 5.50; N, 6.10.

Hydroboration-Isomerization-Oxidation of cis,cis-1,3-Cyclononadiene

The organoborane obtained from cis,cis-1,3-cyclonona-diene (0.61 g, 0.005 mol) and 2.5 ml of 2M borane solution was refluxed in dry tetrahydrofuran for 4 hr. This was oxidized at 0° and worked up as usual. Removal of the solvent yielded 5.15 g (69%) of a solid mp 70° (from benzene-petroleum ether). IR revealed it to be an alcohol. This was identified as cis-1,5-cyclononane diol which gave bis-p-nitrobenzoate[71] (from chloroform-methanol) mp and mixed mp, 182°. Since the isomeric 1,5-cyclononane diols reported in the literature have not been assigned any configuration, an authentic sample of cis-1,5-cyclononane diol was synthesized from 1,2,6-cyclonona-triene by monohydroboration,[70] reduction of 5-cyclononen-1-one with lithium aluminium hydride followed by hydroboration-oxidation of the product, 5-cyclononen-1-ol.[31]

Anal. for $C_9H_{18}O_2$: Calcd: C, 68.30; H, 11.39.

Found: C, 68.94; H, 11.48.

for $C_{23}H_{24}O_8N_2$: Calcd: C, 60.50; H, 5.20; N, 6.14.

Found: C, 60.20; H, 5.40; N, 5.80.

Preparation of cis-5-Cyclononen-1-one

Following the general procedure described for the hydro-
boration, 1,2,6-cyclononatriene (18.0 g, 0.15 mol) in dry tetra-
hydrofuran was hydroborated with 25 ml of 2M borane solution
(0.05 mol) in dry tetrahydrofuran. The crude product isolated
in the usual way was chromatographed on alumina. Elution of
the column with petroleum ether (60-80°) gave 4.5 g of the
starting material. Further elution with petroleum ether-ether
provided 4.0 g of cis-5-cyclononen-1-one, bp 98-100° at 12 mm,
semicarbazone mp 170-171° (lit.[70] bp 95-100° at 14 mm, semi-
carbazone mp 170-171°). The compound showed characteristic
IR absorptions for cis double bond and carbonyl functional
groups.

Preparation of cis-5-Cyclononene-1-ol

In a dry 500 ml three-necked flask equipped with a
reflux condenser, a mechanical stirrer, a dropping funnel and
a mercury bubbler was placed lithium aluminium hydride (0.76 g,
0.02 mol) in 200 ml of dry ether. A solution of cis-5-cyclo-
nonen-1-one (2.7 g, 0.02 mol) in 50 ml of dry ether was added
dropwise with stirring at a rate to maintain gentle refluxing of
ether. After the addition, the reaction mixture was refluxed

for 30 min and allowed to cool. The complex was hydrolyzed
and the excess lithium aluminium hydride was destroyed by drop-
wise addition of water. The resulting reaction mixture was
poured into 500 ml of 10% sulphuric acid solution. The ether
was separated and the residual aqueous phase was extracted with
ether. The combined extract was washed with water, saturated
sodium carbonate solution, and water, and dried over anhydrous
magnesium sulphate. Removal of the solvent afforded 1.02 g (75%)
of cis-5-cyclononen-1-ol, bp 56° at 1 mm. IR of the unsaturated
alcohol showed absorptions at 3500, 1055 and 720 cm^{-1} assigned
to O-H, C-O and cis-double bond respectively. Its p-nitroben-
zoate had mp 117-118° (from methanol).

Anal. for $C_9H_{16}O$: Calcd: C, 77.10; H, 11.40.

　　　　　　　　　　Found: C, 77.00; H, 11.20.

for $C_{16}H_{19}O_4N$: Calcd: C, 66.4?; H, 6.50; N, 4.87.

　　　　　　　　　　Found: C, 66.95; H, 6.09; N, 4.52.

Preparation of cis-1,5-Cyclononane Diol

Following the usual procedure, cis-5-cyclononen-1-ol
(1.4 g, 0.01 mol) in 15 ml of tetrahydrofuran was hydroborated
with 5 ml of 2M borane solution (0.01 mol). The residual hydride
was destroyed with the slow addition of water. The organoborane
obtained was oxidized with alkaline hydrogen peroxide and worked
up as usual. The column chromatographic separation on basic
alumina using benzene-ether gave 1.0 g (63%) of cis-1,5-cyclo-
nonane diol, mp 70°, bis-p-nitrobenzoate[71] mp 182°.

Hydroboration-Oxidation of cis,cis-1,4-Cyclononadiene

Hydroboration-oxidation of cis,cis-1,4-cyclononadiene (1.85 g, 0.015 mol) with 7.5 ml of 2M borane solution gave 1.95 g of viscous oily product which gave three spots on TLC analysis (alumina). The material was chromatographed on basic alumina as before to get 1.05 g (7%) cis-1,3-cyclononane diol, 2.09 g (11%) cis,cis-1,4-cyclononane diol and 1.2 g (50%) cis,cis-1,5-cyclononane diol. These diols were identified by elemental analysis of their bis-p-nitrobenzoates, IR of the diols and mixed mp of their bis-p-nitrobenzoates with authentic samples.

Hydroboration-Isomerization-Oxidation of cis,cis-1,4-Cyclononadiene

The organoborane from cis,cis-1,4-cyclononadiene (0.60 g, 0.005 mol) and 2.5 ml of 2M borane solution was refluxed in dry tetrahydrofuran for 5 hr. Oxidation of the isomerized organoborane gave a single product, identified as cis-1,5-cyclononane diol. TLC indicated the product to be free from other isomeric diols, and the identification was done using an authentic sample.

Hydroboration-Oxidation of cis,cis-1,5-Cyclononadiene

cis,cis-1,5-Cyclononadiene (3.6 g, 0.03 mol) was hydroborated with 15 ml of 2M borane solution, the oxidation of which afforded 4.0 g of a viscous oil. This showed two spots on TLC (Alumina). The crude material was chromatographed on basic alumina in benzene-ether. Elution of the column with ether-benzene (1:3) gave 3.2 g of a solid (67%) which was recrystallized

solid, mp 52-53° (recrystallized from petroleum ether), IR

spectrum of which showed absorptions for alcohol. Elemental

analysis and NMR indicated it to be a bicyclic alcohol, p-nitro-

benzoate of which had mp 111° (recrystallized from methanol).

The compound on oxidation with chromium trioxide in pyridine

gave a ketone, the semicarbazone of which had mp 192°. Based

on these evidences the compound was identified as trans,cis-β-

decalol (lit[87] alcohol mp 53°; p-nitrobenzoate mp 112°; semi-

carbazone of trans-β-decalone mp 192-193°[88]).

Anal. for $C_{10}H_{18}O$: Calcd: C, 77.90; H, 11.68.

Found: C, 77.63; H, 11.64.

for $C_{17}H_{21}O_4N$: Calcd: C, 67.32; H, 6.93; N, 4.62.

Found: C, 67.92; H, 7.17; N, 4.50.

Column was further eluted with 3:2 ether-benzene to

give 0.2 g (9%) of cyclodecane diol (A), mp 66-68; bis-p-nitro-

benzoate, mp 84-85° (recrystallized from chloroform-methanol).

Finally, 0.40 g (18%) of another cyclodecane diol (B) was

obtained from the column on eluting it with ether. This diol (B)

had mp 89-91° (recrystallized from ethyl acetate); bis-p-nitro-

benzoate mp 154-156°.

Anal. for $C_{10}H_{20}O_2$: Calcd : C, 69.76; H, 11.62.

Found (A) : C, 69.60; H, 11.64.

Found (B) : C, 69.53; H, 11.56.

for $C_{24}H_{26}O_8N_2$: Calcd : C, 61.27; H, 5.53; N, 5.95.

Found (A) : C, 61.38; H, 5.50; N, 5.88.

Found (B) : C, 61.10; H, 5.74; N, 5.90.

Product distribution did not change on isomerizing the organoborane from cis,cis-1,3-cyclodecadiene.

Hydroboration-Oxidation of cis,cis-1,6-Cyclodecadiene

cis,cis-1,6-Cyclodecadiene (1.38 g, 0.01 mol) in 20 ml of dry tetrahydrofuran was hydroborated with 5 ml of 2M borane solution. Oxidation with alkaline hydrogen peroxide after the usual work-up afforded 1.4 g (82%) of a solid, which was recrystallized from ethyl acetate and had mp 135-136°. IR spectrum indicated it to be an alcohol and was identified as cis-1,5-cyclodecane diol (bis-p-nitrobenzoate mp 140°, from chloroform-methanol).

Anal. for $C_{10}H_{22}O_2$: Calcd: C, 69.76; H, 11.62.

Found: C, 69.65; H, 11.54.

for $C_{24}H_{26}N_2O_8$: Calcd: C, 61.27; H, 5.53; N, 5.95.

Found: C, 61.20; H, 5.80; N, 5.87.

Hydroboration-Isomerization-Oxidation of cis,cis-1,6-Cyclodecadiene

Hydroboration-isomerization for 70 hr at 70° followed by oxidation of 0.69 g (0.005 mol) of cis,cis-1,6-cyclodecadiene afforded 0.7 g (82%) of cis-1,5-cyclodecane diol. Diol mp and mixed mp 135-136°, bis-p-nitrobenzoate mp 140°.

Hydroboration-Oxidation of cis,trans-1,5-Cyclodecadiene

Hydroboration followed by oxidation of cis,trans-1,5-cyclodecadiene (3.4 g, 0.025 mol) with 12.5 ml of 2M borane solution in dry tetrahydrofuran yielded 3.5 g of a thick oil

which showed three spots on alumina coated plate with ethyl acetate as solvent. This was subjected to column chromatography on basic alumina. Elution of the column with benzene gave 0.30 g of a liquid (8%). GLC analysis on a 5 ft silicone rubber column showed it to be a 1:1 mixture of cyclodecanone and cyclodecanol, on comparison with authentic samples and their derivatives.

Cyclodecanone oxime mp and mixed mp 88° (lit[89] 88°), cyclodecanol-p-nitrobenzoate mp and mixed mp 113-115° (lit[90] 115°). Elution of the column with ether-benzene (1:4) gave 0.4 g (10%) of cis-1,5-cyclodecane diol identical in all respects with the diol obtained from hydroboration-oxidation of cis,cis-1,6-cyclodecadiene.

Further elution of the column with ether yielded 2.7 g of another solid (61%) which was recrystallized from ethyl acetate and had mp 116°. IR showed absorptions for O-H and C-O at 3500 and 1080 cm^{-1} respectively, and was characterized as cis-1,4-cyclodecane diol (bis-p-nitrobenzoate mp 145-146° from chloroform methanol).

Anal. for $C_{10}H_{20}O_2$: Calcd: C, 69.76; H, 11.62.
Found: C, 69.51; H, 11.39.

for $C_{24}H_{26}N_2O_8$: Calcd: C, 61.27; H, 5.53; N, 5.95.
Found: C, 61.30; H, 5.80; N, 5.78.

Hydroboration-Isomerization-Oxidation of cis,trans-1,5-Cyclodecadiene

The organoborane obtained from cis,trans-1,5-cyclodecadiene (1.36 g, 0.01 mol) was isomerized for 5 hr at 70°. This was

oxidized at 0° and worked up as usual. Removal of the solvent afforded 1.2 g (80%) of a liquid, which distilled at 105-110° at 1 mm. GLC analysis on a 5 ft silicone rubber column showed it to be a 1:1 mixture of cyclodecanone and cyclodecanol.

Mass spectra of cis-1,4 and 1,5-cyclononane diols and cis-1,5-cyclodecan diols showed M-18 as a base peak.

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CHAPTER II

REACTION OF BICYCLIC ORGANO-BORANES WITH SILVER NITRATE

II.1 ABSTRACT

The reactions of bicyclic organoboranes from medium-ring dienes, cis,cis-1,5-cyclooctadiene, cis,cis-1,5-cyclononadiene and cis,cis-1,6-cyclodecadiene with silver nitrate in alkaline medium give mainly cyclic ketone and a minor amount of cis-cyclic olefin. It has been demonstrated that the composition of products is dependent on the molar ratio of the diene to silver nitrate used in the reaction, and the nature of the bicyclic organo-borane. Various reasonable mechanistic pathways have been proposed to explain the formation of the products.

II.2 INTRODUCTION

The building up of a desired carbon structure through carbon-carbon linkage can be achieved via organometallics. Accordingly, the possibility of using organoboranes for this purpose has been explored to a limited extent. Silver salts have been found to be quite effective in bringing about the coupling of the alkyl groups of organometallics.

The reaction between diethyl zinc and silver nitrate was reported as early as 1859.[1] The formation of metallic silver and gaseous products was observed in this reaction. Later, organosilver compounds of low thermal stability were prepared by the reaction of organolead, tin or bismuth compounds with silver nitrate.[2-6] However, nothing is still known about the structures of these organosilver compounds and the nature of carbon-silver bond. It has been shown that the perfluoro-alkyl silver compounds obtained by the addition of silver fluoride to fluorine substituted olefins and acetylenes are more stable than the unsubstituted organosilver compounds.

The oxidative dimerization of Grignard reagent with silver bromide to give coupled products in 40-60% yield was reported by Gardner and coworkers.[9-11] Later the stoichiometry as well as catalytic reduction of the silver salt by the Grignard reagent was studied.[12] The dimerization with silver nitrate was found to be unique in that less than stoichiometric amount of silver (I) salt was required, since the nitrate anion was capable of reoxidizing the silver formed (Scheme 1).

Scheme 1

Stoichiometric amount of silver halide:

$$RMgX + AgY \longrightarrow RAg + MgXY$$

Y = Acetate, halide or perchlorate

$$2RAg \longrightarrow R-R + 2 Ag$$
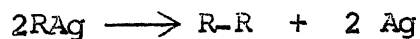
On exposing two Grignard reagents simultaneously:

$$R'Ag + RAg \longrightarrow R'R + R-R + R'-R' + 2 Ag$$

Catalytic amount of silver halide:

$$R'MgX + AgX \longrightarrow R'Ag + MgX_2$$

$$2 R'Ag \longrightarrow R'-R' + Ag$$

$$Ag + RX \xrightarrow{\text{slow}} R\cdot + AgX$$

$$R\cdot + Ag \longrightarrow RAg$$
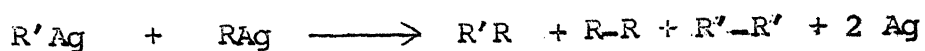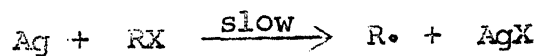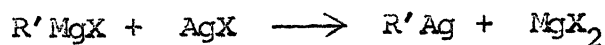
Johnson and coworkers, for the first time, brought about a similar dimerization by treatment of n-butylboronic acid and n-hexylboronic acid with ammoniacal silver oxide to get n-octane and n-dodecane respectively.[13,14] However, Brown and coworkers[15] explored the possibility of coupling the alkyl groups of tri-alkylboranes by treatment with silver halide or Tollen's reagent or silver oxide. They found a remarkable effect of sodium hydroxide on the yield of the coupling product (Scheme 2).

Scheme 2

$$(C_2H_5)_3B \xrightarrow[\text{13 hr, 25°}]{\text{Ag}_2\text{O}} CH_3-CH_2-CH_2-CH_3 + CH_2=CH_2 + CH_3-CH_3$$

9%   5%   15%

$$\xrightarrow[\substack{0° \text{ or } 25°, \\ 30 \text{ min.}}]{\substack{\text{Ag}_2\text{O-} \\ \text{NaOH}}} 72\% + 9\% + 9\%$$
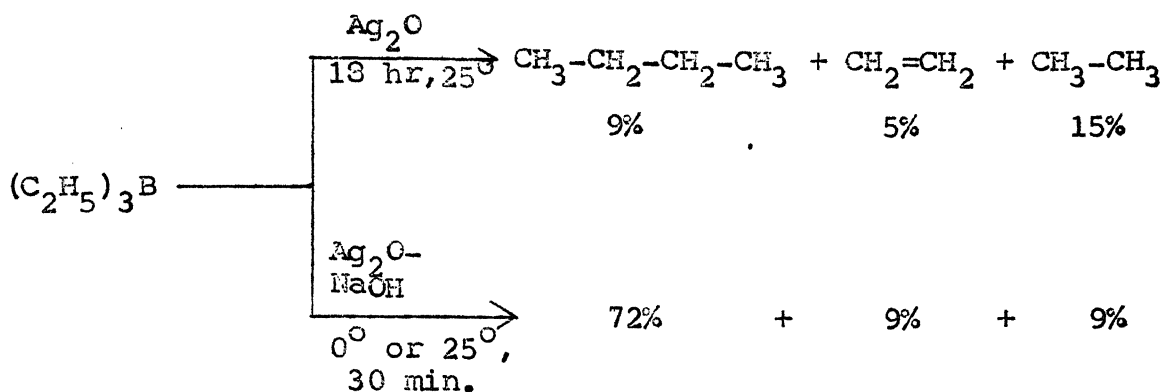
The method was further developed to achieve the coupling of a variety of alkyl groups in high yields directly in the hydroboration flask by mere treatment of the trialkylborane with potassium hydroxide and silver nitrate (Scheme 3).[16]

Scheme 3

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow[\text{2. AgNO}_3 + \text{KOH}]{\text{1. B}_2\text{H}_6} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

$$CH_3-CH_2-CH_2-\underset{\underset{}{|}}{\overset{\overset{CH_3}{|}}{C}}=CH_2 \longrightarrow CH_3-CH_2-CH_2-\underset{\underset{}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-CH_2-\underset{\underset{}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-CH_2CH_3$$

$$CH_3-CH=CH-CH_3 \longrightarrow CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH-CH_2-CH_3$$
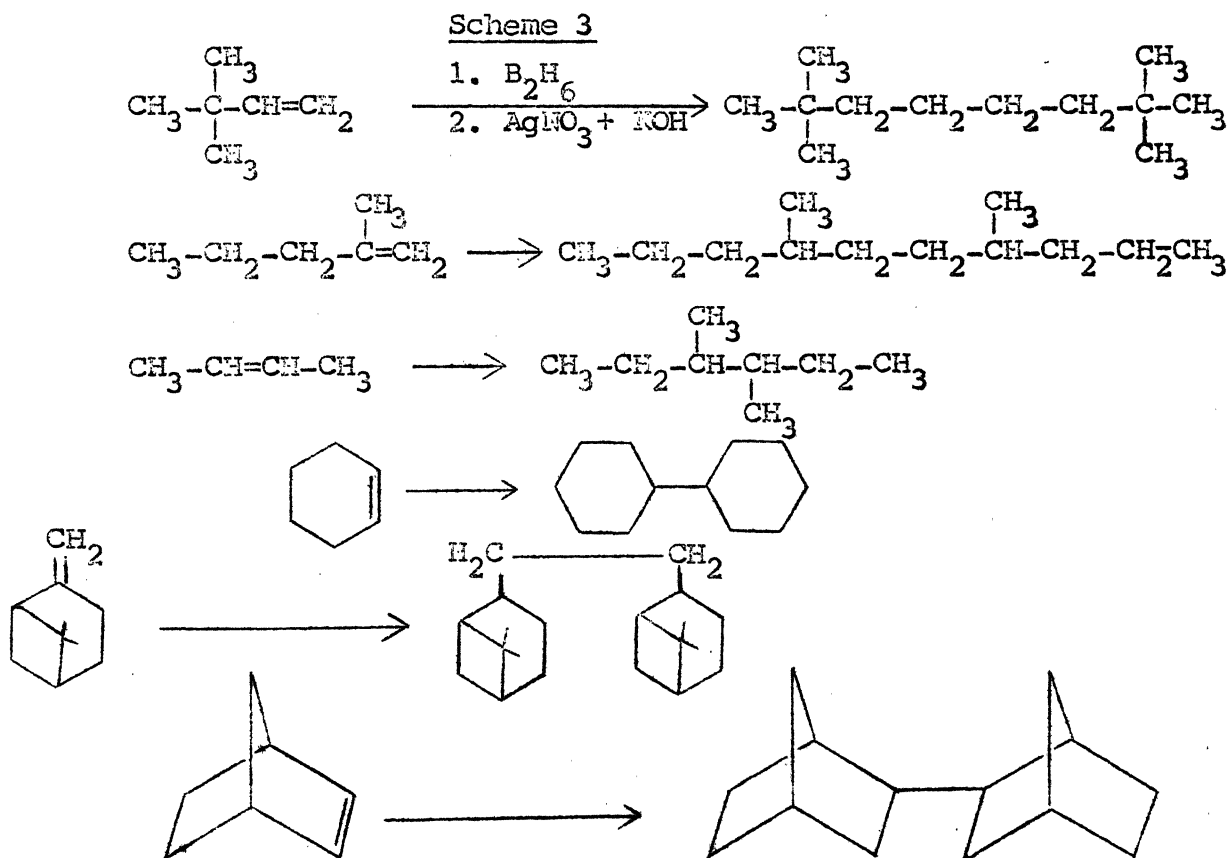
The reaction has also been extended as a means of coup-
ling two different alkyl groups (Scheme 4).[17]

Scheme 4

$$CH_3-CH_2-CH_2-CH_2-CH=CH_2 + CH_3-CH_2-CH_2-CH=CH_2 \xrightarrow[\substack{2.\,AgNO_3 + \\ KOH}]{1.\,B_2H_6} CH_3-(CH_2)_9CH_3$$

$$CH_3-CH_2-CH_2-CH_2-CH=CH_2 \ + \ \text{[cyclopentene]} \longrightarrow \text{[cyclopentyl]}-(CH_2)_5-CH_3$$
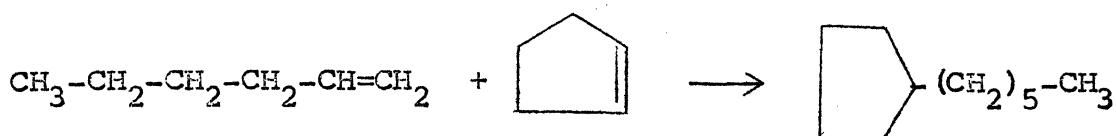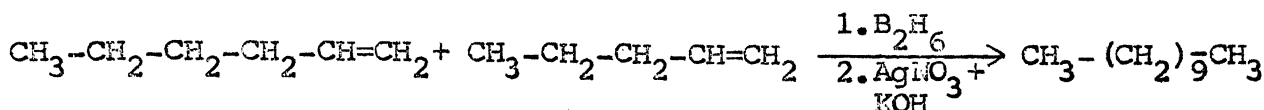
Since hydroboration reaction can tolerate many different
functional groups that are not compatible with Grignard reagent,
this combined procedure of hydroboration-coupling reaction has
been used in the synthesis of a variety of products (Scheme 5).
It has been suggested that the reaction proceeds through silver
alkyl which breaks down into silver and alkyl radical.
The allyl radicals dimerize to form the coupling product.

Scheme 5

$$CH_2=CH-(CH_2)-CO_2C_2H_5 \longrightarrow \begin{array}{l} CH_2-CH_2-(CH_2)_8-CO_2C_2H_5 \\ | \\ CH_2-CH_2-(CH_2)_8-CO_2C_2H_5 \end{array}$$

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 \ + \ CH_2=CH-(CH_2)_8-CO_2C_2H_5 \longrightarrow$$

$$(CH_3)_2CH-CH_2-CH_2-CH_2-(CH_2)_8-CO_2C_2H_5$$
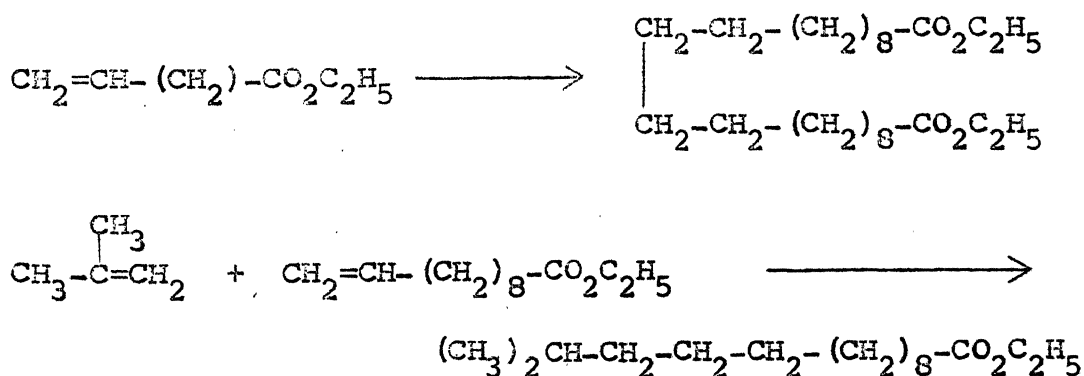
In view of the results obtained from the reactions of trialkyl organoboranes with silver nitrate in presence of potassium hydroxide, we planned to investigate the reactions of bicyclic organoboranes, synthesized by cyclic hydroboration of medium-ring dienes (cis,cis-1,5-cyclooctadiene,cis,cis-1,3-cyclooctadiene, cis,cis-1,5-cyclononadiene and cis,cis-1,6-cyclodecadiene), with silver nitrate and potassium hydroxide to know the fate of the intermediate radical species. It was thought that a diradical species, if formed, might undergo intramolecular coupling to give bicyclic hydrocarbons.

II.3   RESULTS AND DISCUSSION

The cyclic medium-ring dienes used in the present investigation were obtained as already described in the previous chapter. The dienes were hydroborated using a standard solution of borane in dry tetrahydrofuran, the procedure of which has been given in Chapter I.4. The organoboranes resulting from cis,cis-1,5-cyclooctadiene (1) and cis,cis-1,5-cyclononadiene (8) were isomerized before treating with silver nitrate and sodium hydroxide. The organoborane solution in tetrahydrofuran was chilled in ice-salt. Residual hydride was destroyed by the careful addition of water. Addition of silver nitrate was preceeded by sodium hydroxide solution. The black solution obtained on adding silver nitrate deposited silver on stirring for nearly 2 hr. The mixture was extracted with ether. The aqueous layer was neutralized with dilute nitric acid and

extracted with ether. The combined extract was washed with water, and dried over anhydrous magnesium sulphate. Removal of the solvent afforded crude product which was distilled and analyzed by GLC and IR.

cis,cis-1,5-Cyclooctadiene (1) on cyclic hydroboration-isomerization followed by treatment with silver nitrate in 1:1 molar ratio in sodium hydroxide solution yielded cyclooctanone (4) as major product along with a small amount of cyclooctene (3) (Scheme 6). But the use of cis,cis-1,5-cyclooctadiene (1) and silver nitrate in the ratio 1:3 resulted mainly in the formation of cis-cyclooctene (3). The use of a catalytic amount of silver nitrate led to a severe cut on the yield of the products.

Scheme 6
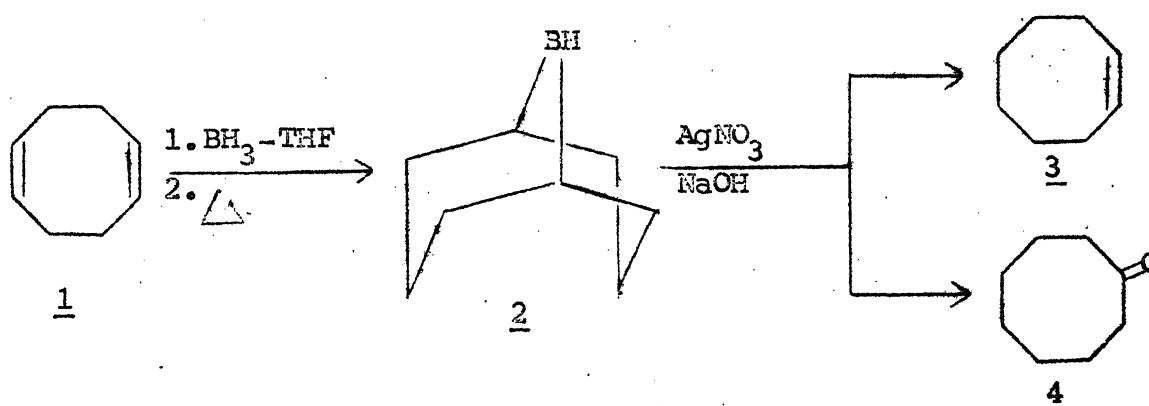
The mixture of bicyclic organoboranes (6 and 7) from cis,cis-1,3-cyclooctadiene (5) on treatment with silver nitrate in the molar ratio 1:1 in the presence of sodium hydroxide gave 85% of cis-cyclooctene (3) and 15% of cyclooctanone (4) (Scheme 7).

Scheme 7
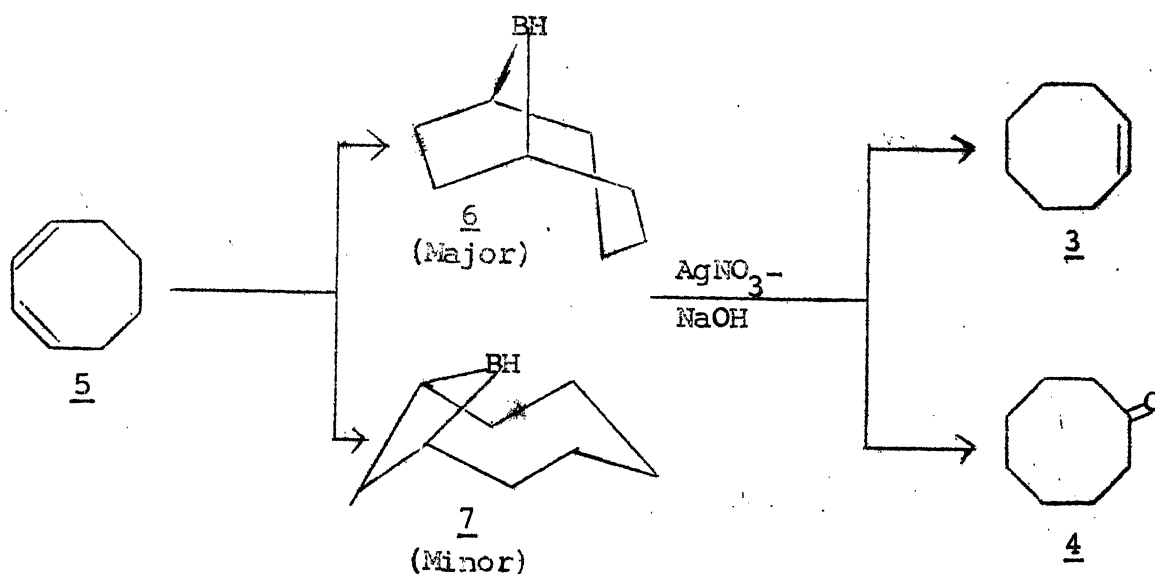
cis,cis-1,5-Cyclononadiene (8) and cis,cis-1,6-cyclode-cadiene (12) behaved very similar to cis,cis-1,5-cyclooctadiene (1) in its reaction with silver nitrate in the ratio 1:1. The 10-borabicyclo(4.3.1)decane (9) obtained from hydroboration-isomerization of 8 yielded a mixture of cis-cyclononene (10) and cyclononanone (11) in the ratio 15:85, whereas 11-borabicyclo-(5.3.1)undecane (13) from 12 resulted in a mixture of cis-cyclo-decene (14) and cyclodecanone (15) in the ratio 1:9 (Scheme 8).

The cyclic olefin and the cyclic ketone were separated by preparative GL^C and identified by comparison of GLC retention times and I^R with authentic samples.

The reaction between trialkylborane and silver nitrate in alkaline medium has been suggested to give organosilver compound (16) which undergoes homolytic carbon-silver bond cleavage to produce hydrocarbon radical (17) and silver. The formation of

Scheme 8
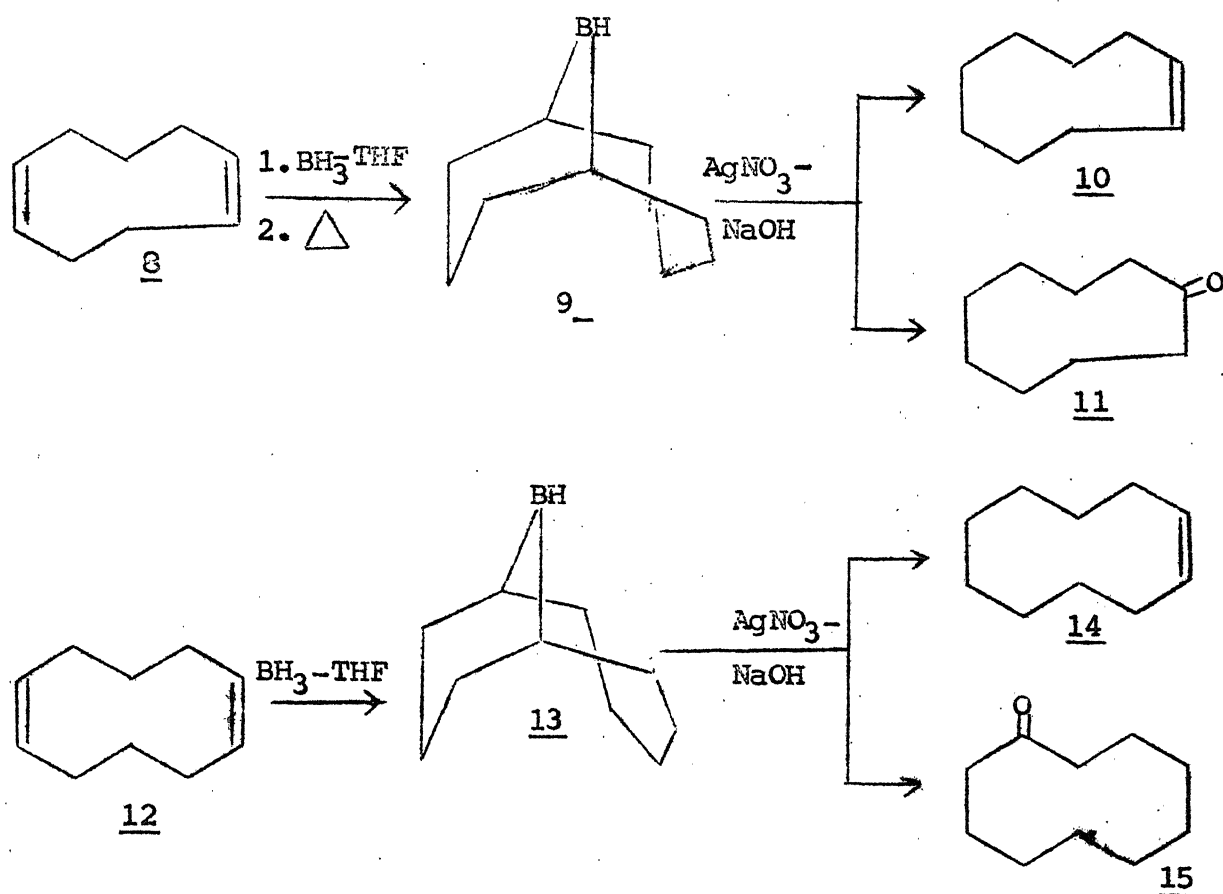
alkane (18) has been explained as due to the combination of the intermediate free radical species (17) (Scheme 9).

Scheme 9

$$>B-R \ + \ Ag-OH \ \longrightarrow \ R-Ag \ + \ >B-OH$$
$$\underline{16}$$

$$R-Ag \ \longrightarrow \ R\cdot \ + \ Ag^{0}$$
$$\underline{17}$$

$$2 \ R\cdot \ \longrightarrow \ R-R$$
$$\underline{17} \qquad\qquad \underline{18}$$
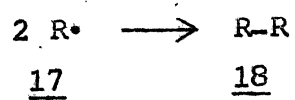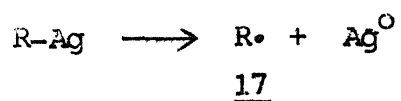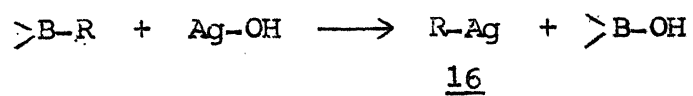
Our results on the reaction of bicyclic organoboranes
with silver nitrate and sodium hydroxide point out, first of
all, that the three bicyclic organoboranes, 2, 9 and 13 behave
similarly producing mainly cyclic ketone with a small amount
of cis-cyclic olefin when the cyclic diene and silver nitrate
are used in 1:1 molar ratio. The composition of the products
is dependent on the molar ratio of diene/silver nitrate. Further-
more, the results with 1,3-cyclooctadiene (5) reveal that the
composition of the products is also dependent on the nature of
the bicyclic organoborane.

The possible pathways for the formation of cyclooctanone (4)
and cis-cyclooctene (3) from the 9-borabicyclononanes (2 and 6)
are represented in Scheme 10. First, the reaction of 2 with
water gives 19 which leads to the formation of organoboron
silver compound (20) on reaction with silver hydroxide. The
homolytic cleavage of carbon-silver bond in 20 can result in
the formation of radical species (30A) which can give rise to
gem-organoboron radical (31) by 1,5-hydrogen shift or vic-organo-
boron radical (32) by 1,4-hydrogen shift. Electronically, the
odd electron on carbon in 31 or 32 can be delocalized with the
electrophilic boron to form 33 and 34 respectively. The composi-
tion of the 31 & 32 from 30 (A & B) in the reaction may be dictated
by the favourable transition state involved in the formation of
the radical concerned after the homolytic cleavage of the carbon-
silver bond or/and their thermodynamic stabilities. The inter-

conversion of 31 and 32 is possible by 1,2-hydrogen shift. The
radical species (31 and 32) can take different paths as shown
in the Scheme 10 to yield cyclooctanone (4) and cis-cyclooctene
(3) respectively. If the paths A and B for the geneses of
4 and 3 respectively were to be the real ones, one would expect
the liberation of an equivalent amount of hydrogen. However,

Scheme 10
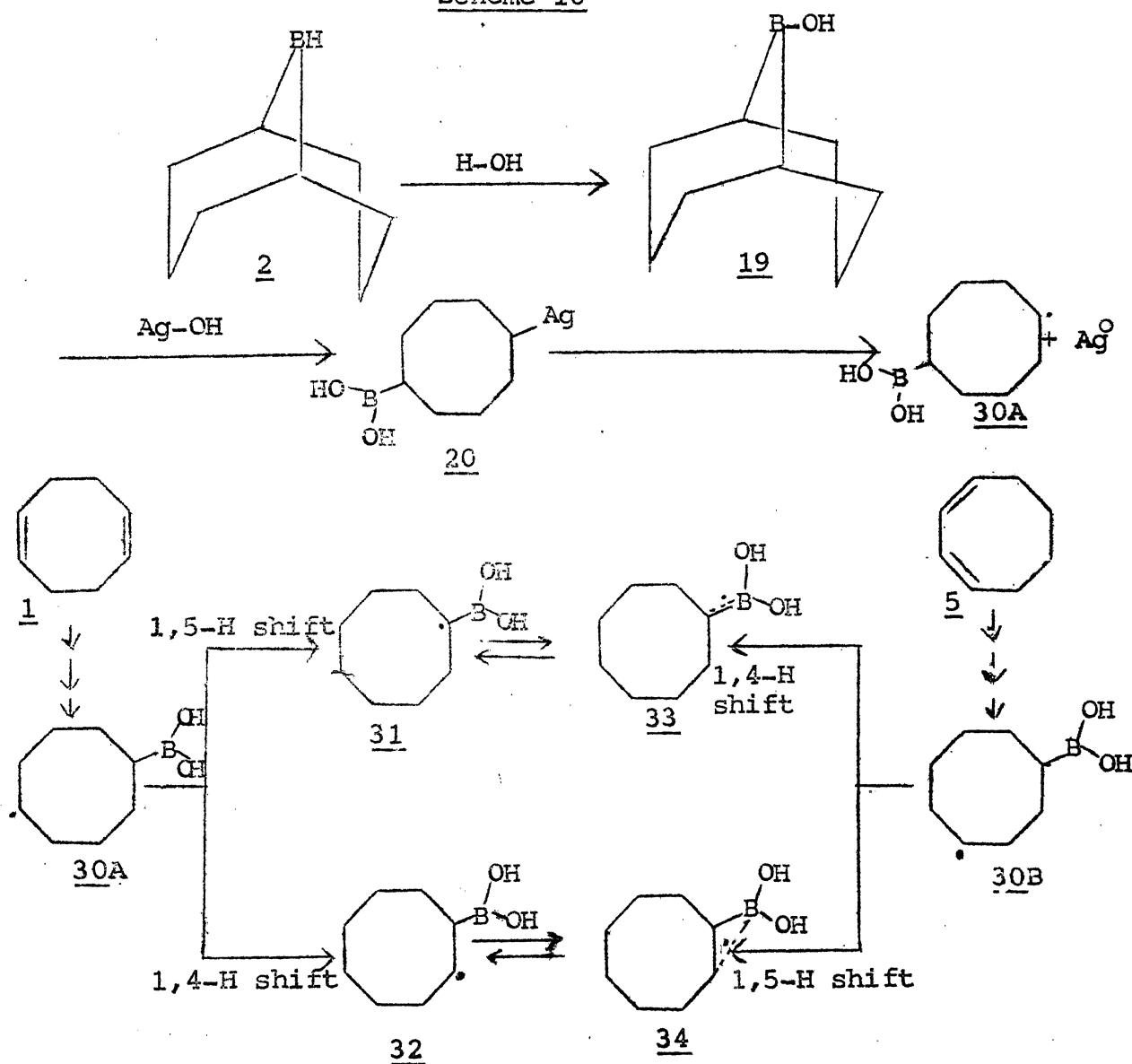
Scheme contd.
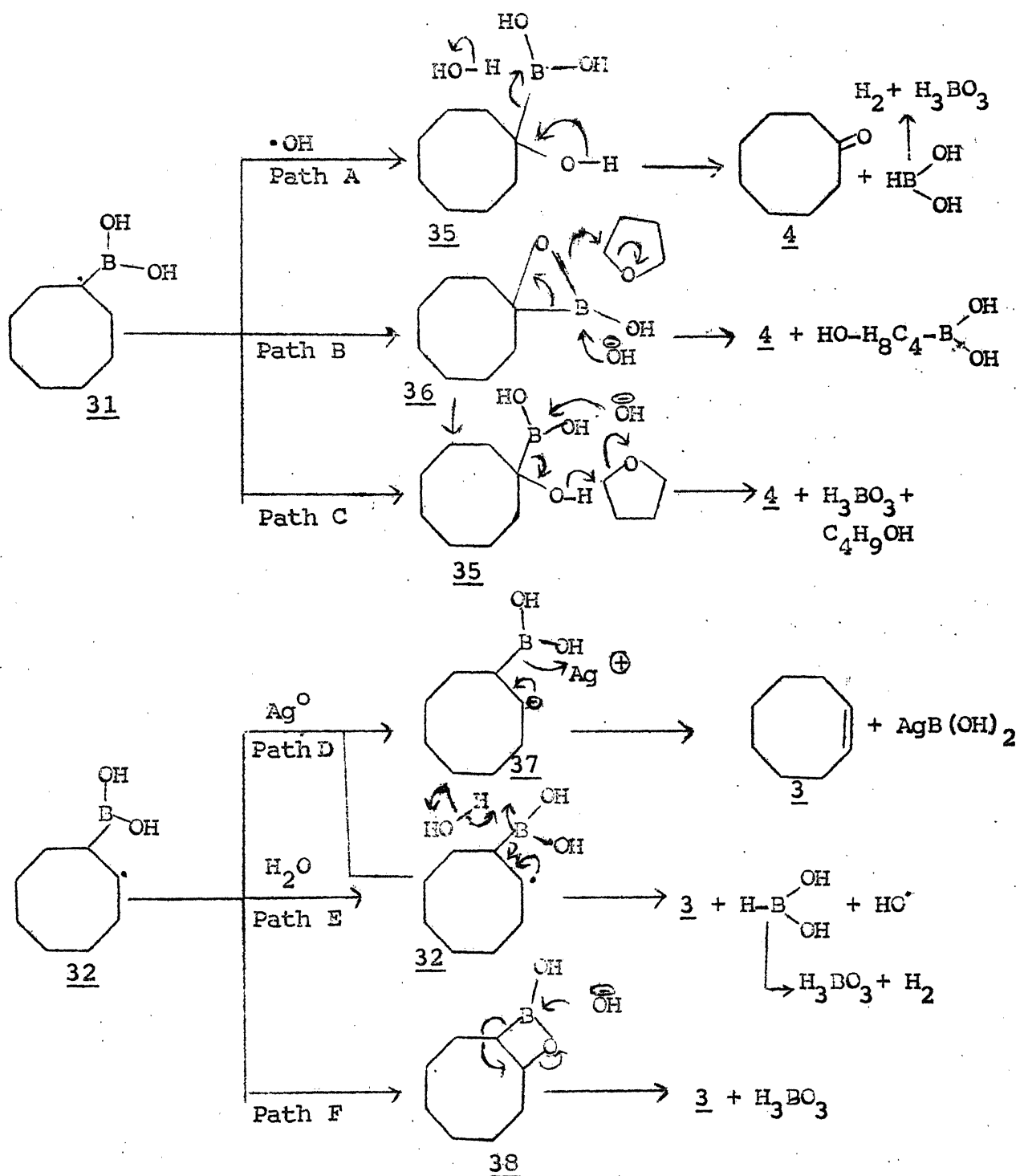
no hydrogen was evolved during the reaction. Hence, the paths A and E have been ruled out. The paths B and C involve the solvent molecule, tetrahydrofuran. It is possible to check the validity of these paths by isolating all the products of such reactions.

The path D proposed for the formation of $\underline{3}$ involves the oxidation of metallic silver to silver ($\underline{1}$) ion, whereas the path F involves the oxyborohetcrocyclic intermediate ($\underline{38}$).

We propose the diradical intermediates ($\underline{39}$ and $\underline{40}$) when the 9-borabicyclononanes ($\underline{2}$ and $\underline{6}$) are treated with excess of silver nitrate, which lead to the preferential formation of cis-cyclooctene ($\underline{3}$) (Scheme 11). Similar pathways could be proposed to explain our results with other medium-ring dienes.

Scheme 11
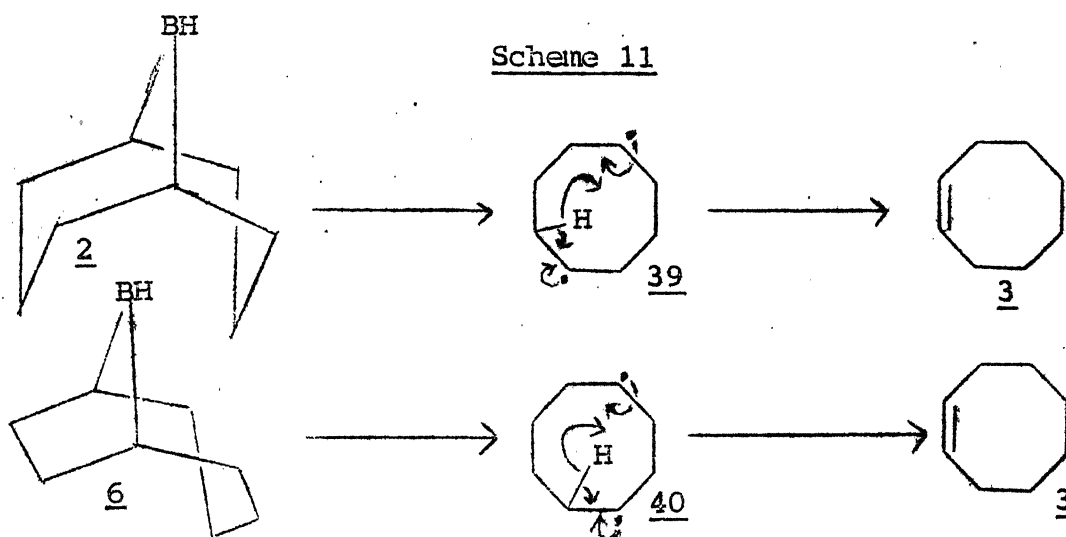
In conclusion, this study is interesting in the sense that it demonstrates how the reaction in medium-ring systems could take completely different routes from the normal paths observed in the case of acyclic systems.

II.4   EXPERIMENTAL

All boiling points are uncorrected. The infrared (IR) spectra were recorded on a Perkin-Elmer Model-700 spectrophotometer as liquid film between sodium chloride plates. Gas liquid

chromatographic analyses were made with Aerograph Model-90P
instrument using 10 ft x 1/4 inch carbowax or 5 ft x 1/4 inch
silicone rubber column.

Starting Materials

Silver nitrate (BDH) and potassium hydroxide (BDH) were
used as such. All other materials used were the same as described
earlier in Chapter I.4.

Preparation and Reaction of 9-Borabicyclo(3.3.1)nonane with Silver Nitrate-Potassium Hydroxide

In a 250 ml 3-necked flask equipped with a pressure-
equalising dropping funnel, a low temperature thermometer and
an inlet and an outlet for dry nitrogen, was placed 15 ml of
2M borane solution (0.03 mol). A solution of cis,cis-1,5-cyclo-
octadiene (3.24 g, 0.03 mol) in 90 ml of dry tetrahydrofuran was
added through the dropping funnel over a period of 30 min. The
temperature of the flask was maintained between 0-5°. After
allowing it to stir for half an hour more at that temperature, it
was stirred for 2 hr at room temperature and 4 hr at 70° (reflux-
ing THF). The mixture was cooled to 10° and hydrolysed carefully
with water. This was treated with potassium hydroxide (3.4 g,
0.06 mol) in 30 ml of water and silver nitrate (5.1 g, 0.03 mol)
in 30 ml of water. The mixture was allowed to stir for 2 hr.
There was a deposit of silver on the sides of the flask. The
solution was extracted with ether, washed with dilute nitric acid,
sodium carbonate solution and finally with water. The extract

was dried over anhydrous magnesium sulphate. Removal of the solvent followed by molecular distillation yielded 1.85 g (60%) of a liquid mixture, bp 80-85° (bath temperature) at 70 mm. GLC analysis indicated it to be a mixture of cis-cyclooctene and cyclooctanone in the ratio 17:83. These were separated by preparative GLC and identified by comparison of GLC retention times and IR spectra using authentic samples.

A similar treatment of the isomerized organoborane obtained from cis,cis-1,5-cyclooctadiene (3.24 g, 0.03 mol) and 15 ml of 2M borane solution (0.03 mol) with silver nitrate (15.3 g, 0.09 mol) in 45 ml of water and potassium hydroxide (10.18 g, 0.18 mol) in 60 ml of water afforded 1.65 g (51%) of a liquid mixture containing cis-cyclooctene and cyclooctanone in the ratio 91:9 by GLC analysis.

The reaction of the isomerized organoborane made from cis,cis-1,5-cyclooctadiene (3.24 g, 0.03 mol) and 15 ml of 2M borane solution (0.03 mol) with silver nitrate (0.51 g, 0.003 mol) in 5 ml of water and potassium hydroxide (3.4 g, 0.06 mol) in 30 ml of water gave 0.2 g (6%) of a liquid mixture containing cis-cyclooctene and cyclooctanone in the ratio 15:85.

Preparation and Reaction of 9-Borabicyclo(4.2.1)nonane and 9-Borabicyclo(5.1.1)nonane with Silver Nitrate-Potassium Hydroxide

Following the procedure described for the hydroboration of cis,cis-1,5-cyclooctadiene, cis,cis-1,3-cyclooctadiene (3.24 g, 0.03 mol) was hydroborated with 15 ml of 2M borane (0.03 mol)

solution in 90 ml of dry tetrahydrofuran. The mixture was stirred for 4 hr at room temperature after destroying the residual hydride with 5 ml of water. The mixture was then treated with 10 ml solution of potassium hydroxide (3.3 g, 0.06 mol) and 10 ml solution of silver nitrate (5.1 g, 0.03 mol), and allowed to stir for 2 hr. The usual workup procedure yielded 1.95 g (60%) of a liquid product, bp 75-80° (bath temperature) at 60 mm. GLC analysis on a 10 ft carbowax column showed it to be a mixture of cis-cyclooctene and cyclooctanone in the ratio 9:1. The products were identified using authentic samples as described earlier.

Preparation and Reaction of 10-Borabicyclo(4.3.1)decane with Silver Nitrate-Potassium Hydroxide

cis,cis-1,5-Cyclononadiene (1.22 g, 0.01 mol) was hydroborated with 5 ml of 2M borane (0.01 mol) solution in dry tetrahydrofuran as described earlier in the hydroboration of cis,cis-1,5-cyclooctadiene. The mixture was stirred for 4 hr at 70° and cooled to 10°. Residual hydride was destroyed by adding 5 ml of water. The organoborane was then treated with 10 ml solution of potassium hydroxide (1.12 g, 0.02 mol) and 10 ml of silver nitrate (1.7 g, 0.01 mol) solution. The mixture was allowed to stir for 2-3 hr and worked up in the usual manner to give 1 g (82%) of a liquid, bp 80-85° (bath temperature) at 6 mm. GLC analysis indicated the liquid product to be a mixture of cis-cyclononene and cyclononanone in the ratio 15:85. Both the compounds were separated by preparative GLC and identified using authentic

samples by comparison of GLC retention times and IR spectra.

Preparation and Reaction of 11-Borabicyclo(5.3.1)undecane with
Silver Nitrate-Potassium Hydroxide.

The organoborane obtained from cis,cis-1,6-cyclodecadiene

(1.36 g, 0.01 mol) and 5 ml of 2M borane (0.01 mol) solution in

30 ml of dry tetrahydrofuran was treated with 10 ml solution of

potassium hydroxide (1.12 g, 0.02 mol) and 10 ml solution of

silver nitrate (1.7 g, 0.01 mol). There was an immediate deposi-

tion of silver on the sides of the flask. The mixture was allowed

to stir for about 2 hr. The usual workup procedure gave 0.95 g

(70%) of a liquid, bp 80-85° (bath temperature) at 1 mm. GLC

analysis on a 5 ft silicone rubber column showed the presence of

cis-cyclodecene and cyclodecanone in the ratio 1:9. The products

were identified by comparison of GLC retention times and IR spectra

with authentic samples after preparative GLC separation.

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CHAPTER III

DIHYDROBORATION OF ALLENES

III.1 ABSTRACT

The study on the dihydroboration of some cyclic (1,2-cyclotridecadiene and 1,2-cyclononadiene) and acyclic (3-ethyl-1,2-pentadiene, 3-phenyl-1,2-butadiene and phenylpropadiene) allenes is described. For example, dihydroboration-oxidation of 1,2-cyclotridecadiene gave a mixture of products containing isomeric cyclotridecenes, bicyclo(10.1.0)tridecane, cyclotridecanone, cyclotridecanol, isomeric 1,2-cyclotridecane diols and isomeric 1,3-cyclotridecane diols. However, dihydroboration-hydrolysis-oxidation of 1,2-cyclotridecadiene afforded mainly cyclotridecanol, while dihydroboration-oxidation with chromium trioxide-pyridine yielded a mixture of cis- and trans-cyclotridecene. Reasonable mechanistic pathways have been suggested for the formation of these products. The results with other allenes have also been rationalized on a similar basis.

III.2 INTRODUCTION

Surprisingly few investigations have been described in
the literature on the hydroboration study of allenes as compared
to the isomeric acetylenes. Monohydroboration of cyclic allenes[1]
with diborane followed by oxidation was first reported in 1963.
1,2-Cyclononadiene on monohydroboration-oxidation gave mainly
cyclononanone and smaller amounts of cis-cyclononene and cyclo-
nonenol (Scheme 1). 1,2,6-Cyclononatriene and 1,2-cyclodecadiene
behaved similarly. The formation of ketone as the major product
in these cases points out towards the central attack of boron
in cyclic allenes.

Scheme 1
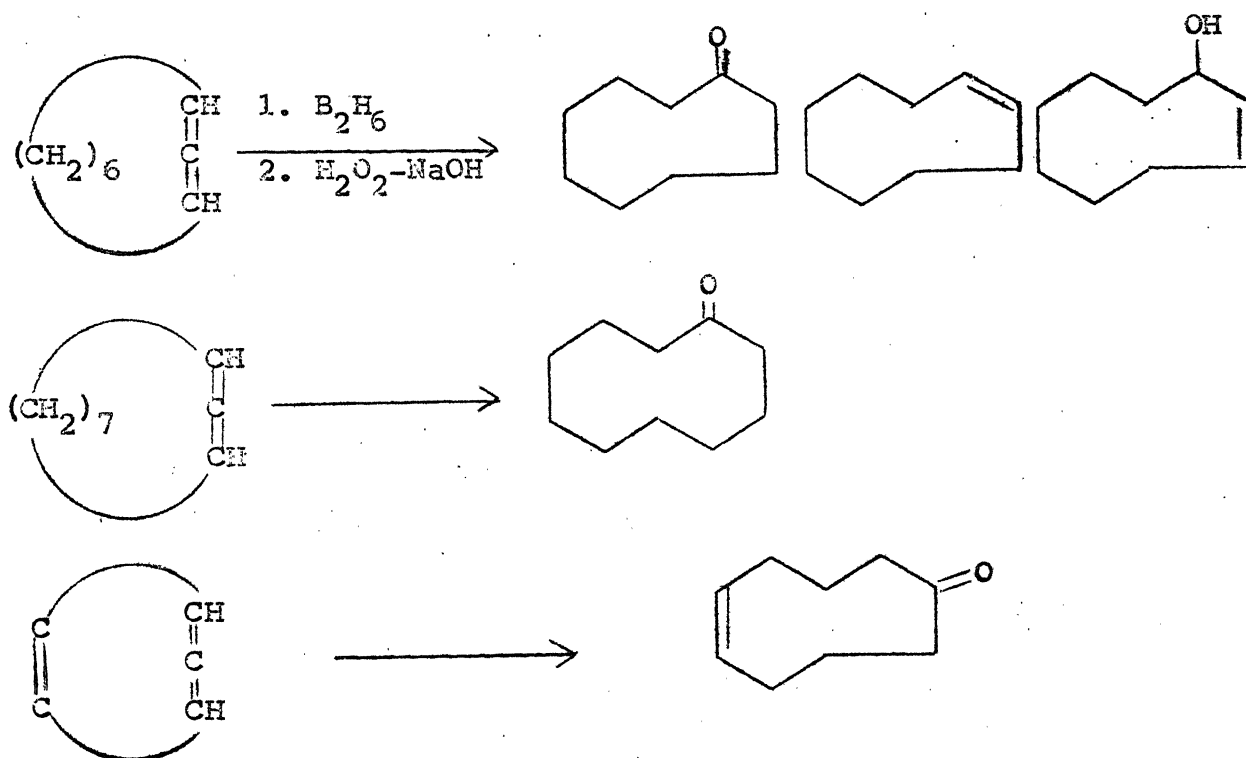
Since diborane is a multifunctional reagent, monohydro-
boration of allenes with diborane might proceed through mono-
alkyl-, dialkyl- and trialkylborane stages. Therefore,
it follows that the transition state for each step in the reac-
tion may have different steric requirements. Thus, the percentage
electrophilic attack of diborane at the central and terminal
carbon atoms of the allenic linkage will be governed by the
cumulative steric effect due to ring size of the allene and the
intermediate organoboranes.

Quite recently, monohydroboration of 3-methyl-1,2-buta-
diene, 2,3-pentadiene, 2,4-dimethyl-2,3-pentadiene & 1,2-cyclonona-
diene has been studied by Fish[2] using 4,4,6-trimethyl-1,3-dioxa-
2-borinane (TMDB) as hydroborating agent, a unifunctional borane
(Scheme 2). The unusual stability of TMDB and its derivatives
has permitted the isolation of allene adducts and thereby, elimi-
nates the usual oxidation step which Brown and coworkers[3] have
employed to detect the point of boron attack.

These results clearly demonstrate the predominant terminal
attack of boron with 1,1-disubstituted and monosubstituted allenes,
and preferential attack on central carbon atom with 1,3-di- and
tetrasubstituted allenes. Similar results have been obtained
with acyclic allenes such as 1,2-nonadiene, phenylpropadiene,
3-phenyl-1,2-butadiene, 4,5-nonadiene & 2,4-Dimethyl-2,3-pentadiene
when disiamylborane was used as the hydroborating agent.[4] These
results have been explained in terms of steric effects on a
four-centered transition state.

Scheme 2

4,4,6-Trimethyl-1,3-dioxa-2-borinane =

(TMDB)

$CH_2=C=CH_2$ $\xrightarrow{\text{TMDB}}$ $CH_2=CH-CH_2-B\!<$

Major product (86%)

$CH_3-CH=C=CH_2$ $\longrightarrow$ $CH_3-CH=CH-CH_2-B\!<$

Major product (78%)

$CH_3-CH=C=CH-CH_3$ $\longrightarrow$ $CH_3-CH=\underset{\underset{/\backslash}{B}}{C}-CH_2-CH_3$

Major product (81%)

$\longrightarrow$ (100%)

$\longrightarrow$

(100%) (cis:trans = 85:15)
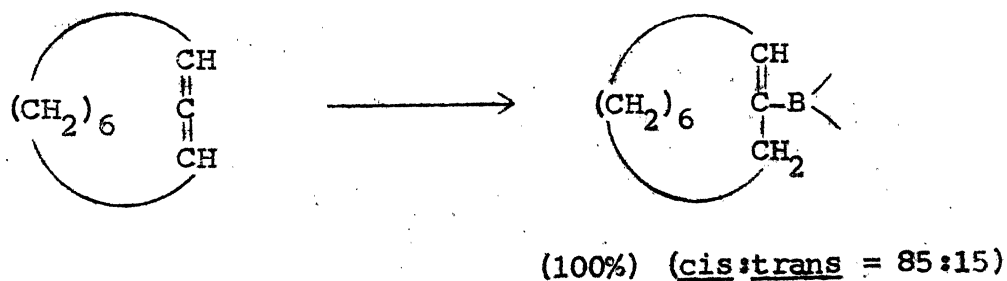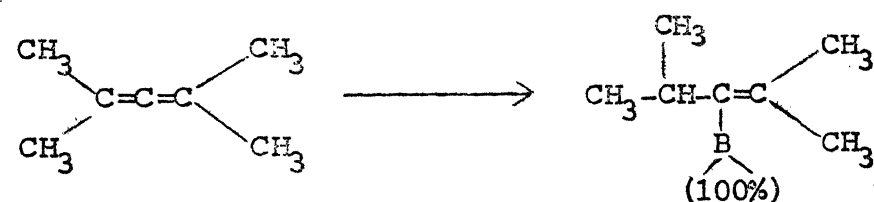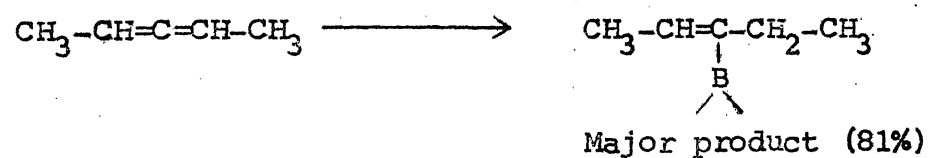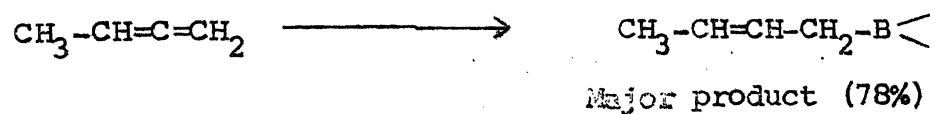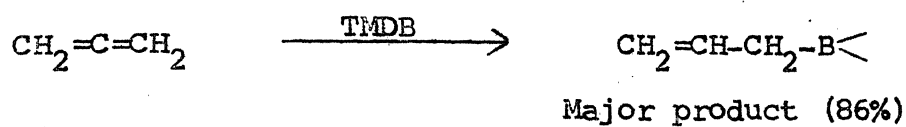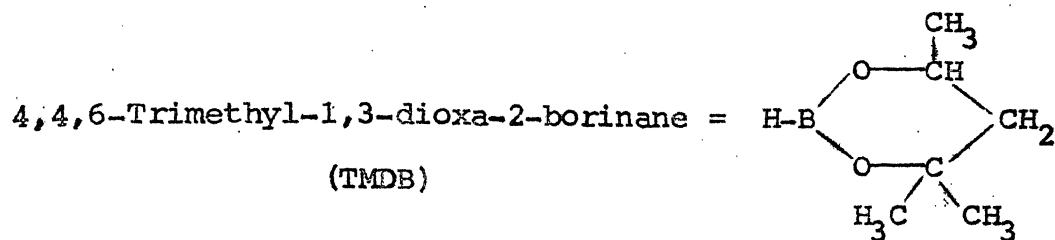
The results on the monohydroboration of cyclic allenes (1,2-cyclononadiene and 1,2-cyclotridecadiene) with disiamylborane are interesting.[5] It has been shown that 1,2-cyclononadiene and 1,2-cyclotridecadiene undergo 78% and 100% hydroboration respectively. 1,2-Cyclononadiene gave products which represented 83% attack of boron at the central carbon atom and 17% attack at the terminal carbon atom. 1,2-Cyclotridecadiene gave 62% central carbon attack and 38% terminal carbon attack (Scheme 3). It is interesting to note that with the increase in ring size, terminal attack of boron increases. The reactivity and selectivity have been explained in terms of steric effects on a four-centered transition state.

Scheme 3

$$R = -CH-CH \begin{smallmatrix} CH_3 \\ CH_3 \\ CH_3 \end{smallmatrix}$$
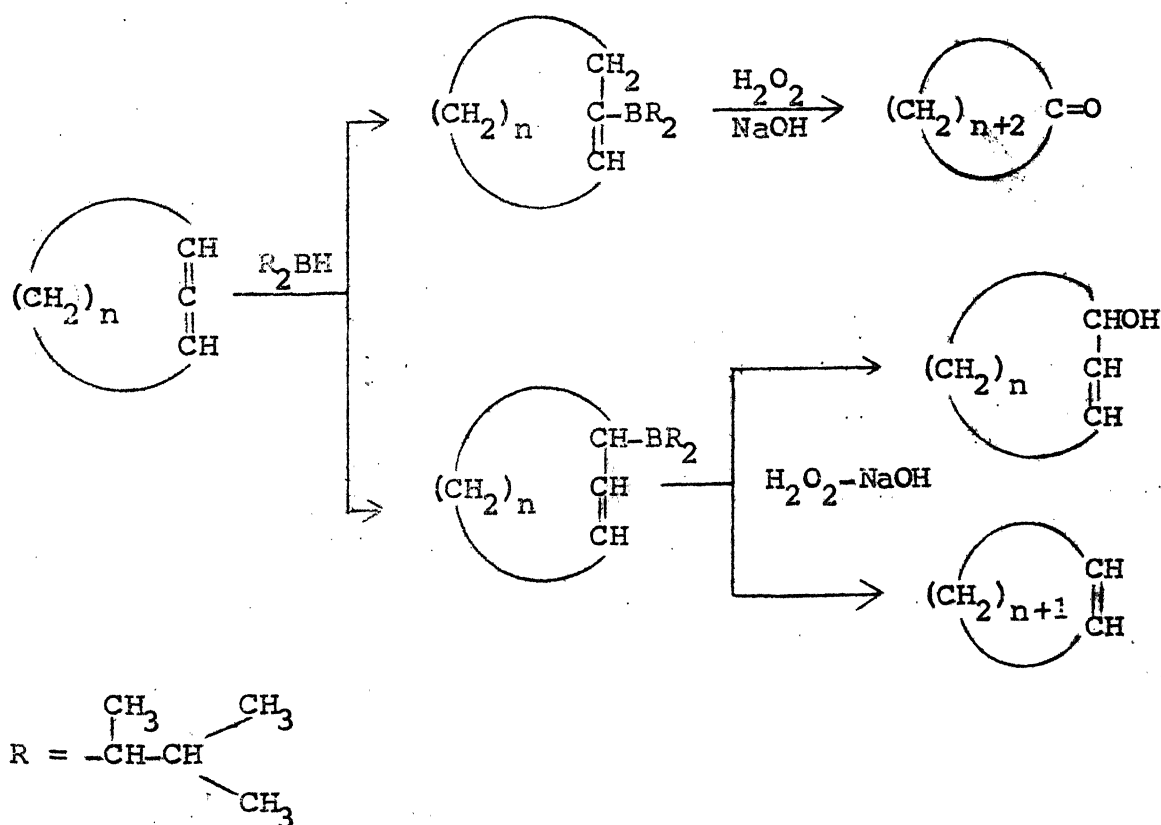
Corsano[6] has reported the dihydroboration of propadiene, 1,2-heptadiene and phenylpropadiene with diborane. Propadiene gave 98% 1,3-propane diol, whereas 1,2-heptadiene and phenylpropadiene yielded a mixture of 1,2- and 1,3-diols after oxidation of the intermediate organoboranes (Scheme 4).

Scheme 4

$$CH_2=C=CH_2 \xrightarrow[\text{2. } H_2O_2-NaOH]{\text{1. } B_2H_6} HOCH_2-CH_2-CH_2OH$$

$$CH_3-CH_2-CH_2-CH_2-CH=C=CH_2 \begin{cases} \longrightarrow CH_3-(CH_2)_3-\underset{\underset{OH}{|}}{C}H-CH_2-CH_2OH \\ \\ \longrightarrow CH_3-(CH_2)_3-CH_2-\underset{\underset{OH}{|}}{C}H-CH_2OH \end{cases}$$

$$C_6H_5-CH=C=CH_2 \longrightarrow C_6H_5-\underset{\underset{OH}{|}}{C}H-CH_2-CH_2OH + C_6H_5-CH_2-\underset{\underset{OH}{|}}{C}H-CH_2OH$$
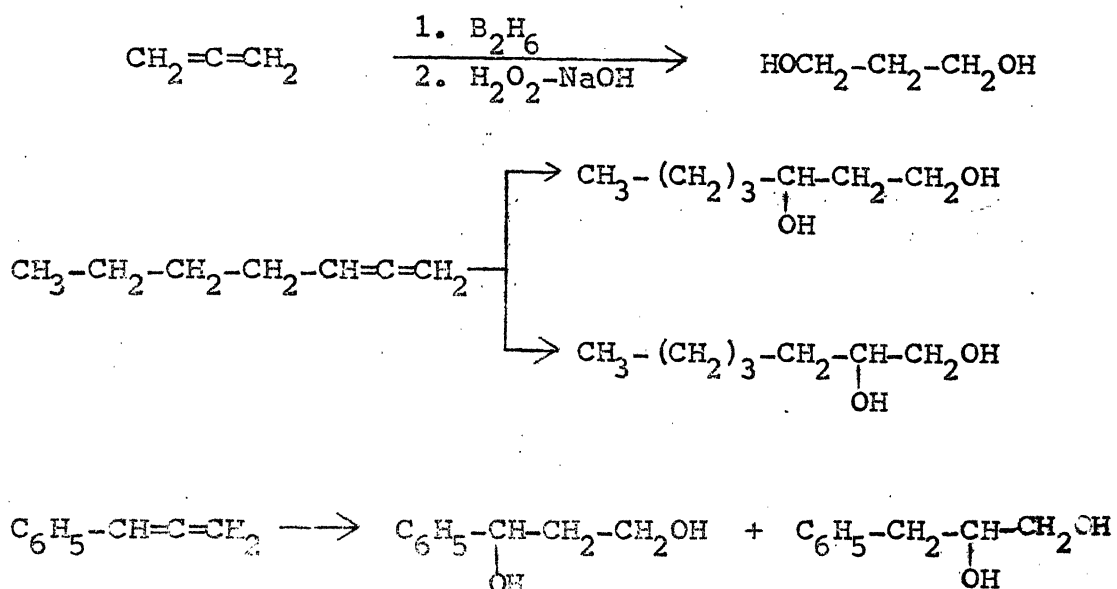
The gas phase reaction of propadiene with excess diborane at 90-95°C has been shown to result in the formation of 1,2-trimethylenediborane or its polymer through allyldiborane[7] (Scheme 5).

It is desirable to review here the hydroboration of acetylenes, as the isomeric acetylenes and allenes are capable of giving rise to some common intermediates on addition of boron-hydrogen bond(s). Monohydroboration-oxidation of a terminal acetylene gives the corresponding aldehyde, while an internal

Scheme 5

$$CH_2=C=CH_2 \; + \; B_2H_6 \longrightarrow CH_2=CH-CH_2-B_2H_5$$
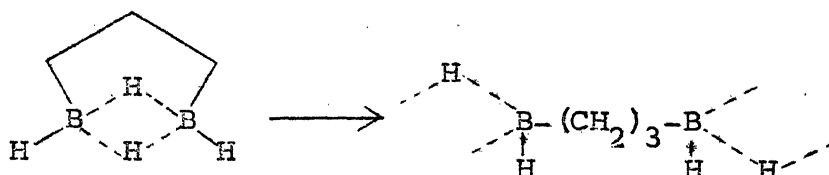
acetylene yields the ketone. The protonolysis of the intermediate vinyl organoborane gives either terminal olefin or cis-olefin in 98-100% purity[3,8,9] (Scheme 6).

Scheme 6

R = Alkyl group

$$Sia = CH_3-CH-CH-CH_3$$
$$\qquad\qquad CH_3$$
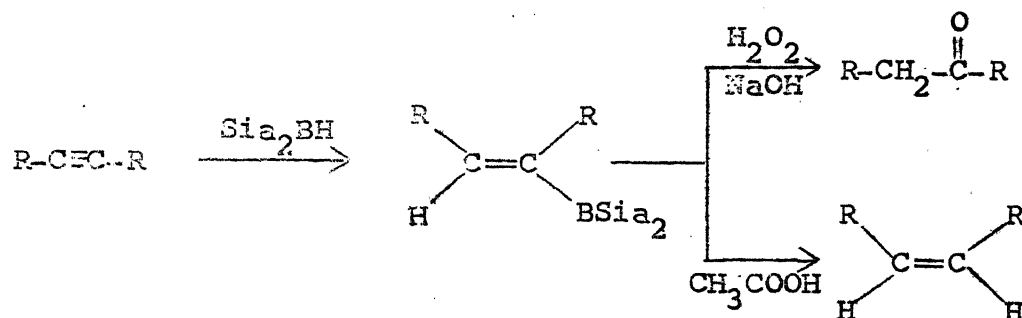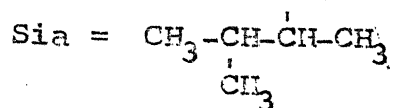
The vinyl organoboranes obtained by the monohydroboration of acetylenes have been utilized in the synthesis of vinyl halides and conjugated dienes.[10-12] Vinylboranes prepared from terminal

acetylenes are readily attacked by bromine. The resulting dibromo-compound eliminates Br-B⟨ moiety by _cis-_ or _trans_-fashion depending on the prevailing conditions to yield bromo-olefin. The trivinylborane from internal acetylenes with iodine leads to stereoselective synthesis of conjugated dienes.

Dihydroboration of terminal acetylenes is known to give gem-diboro compound as the major product, while internal acetylenes give mainly vic-diboro compound[13-16] (Scheme 7). The alkaline hydrolysis of gem and vic-diboro compounds has been studied to a great length by Pasto.[15] Based on deuterium incarpo-ration, it has been suggested that the vic-diboro derivative undergoes exceedingly rapid base-catalyzed hydrolysis. The possibility of neighbouring boron participation during the hydrolysis of vic-diboro compound has been explored. The proposed bridged boron anion is capable of undergoing hydrolysis to give mono-boroderivative, which on oxidation gives alcohol or it can undergo elimination to give olefin (Scheme 7).

Scheme 7
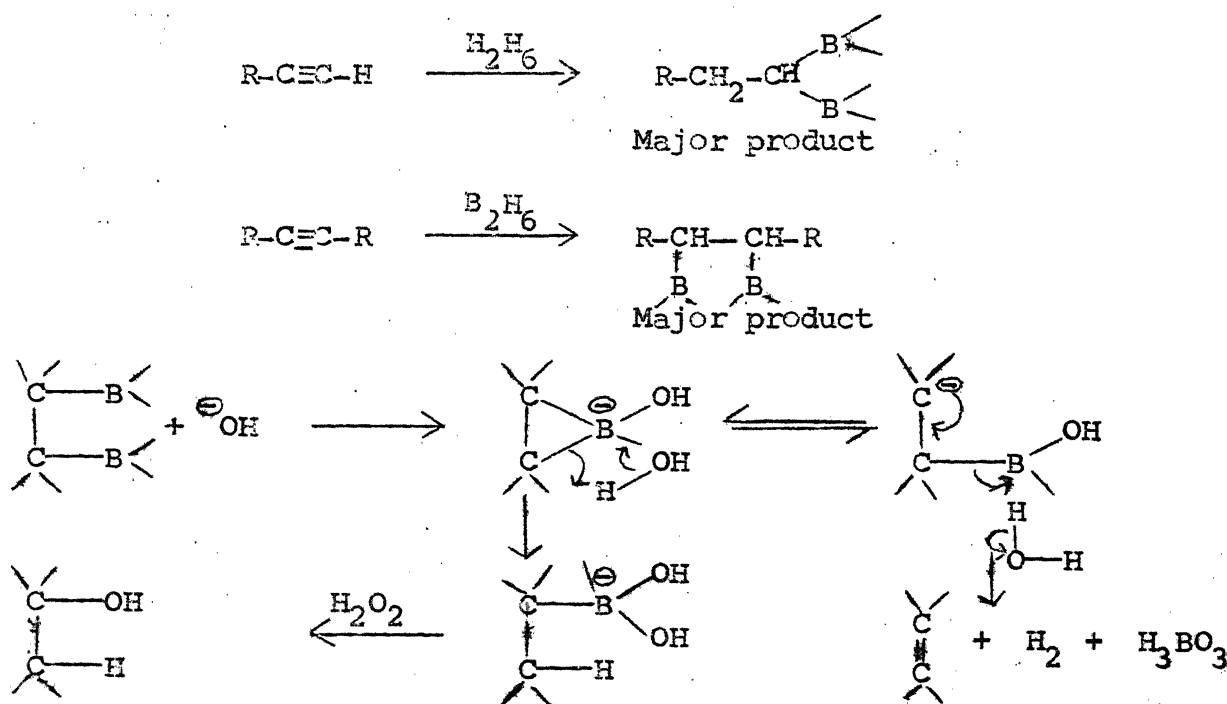
In view of the limited work by Corsano on the dihydrobora-
tion of propadiene and monosubstituted acyclic allenes (1,2-hepta-
diene and phenylpropadiene), it seemed to be of interest to study
the dihydroboration of some acyclic and cyclic allenes. Our work
on the monohydroboration of representative acyclic allenes and
cyclic allenes prompted our entry into this area.

III.3 RESULTS AND DISCUSSION

The allenes (1,2-cyclotridecadiene, 1,2-cyclononadiene,
3-ethyl-1,2-pentadiene, 3-phenyl-1,2-pentadiene and phenylpropa-
diene) required for the present investigation were prepared by
the well known two-step synthesis starting from a suitable olefin
in each case.[17,18] In this two-step sequence, the first step
involves the addition of dibromocarbene to an olefin (1) and the
second step involves the reaction of the resulting 1,1-dibromo-
cyclopropane derivative (2) with methyllithium in ether at -40 to
-45° to obtain allene (3) in good yield (Scheme 8). Thus, the
overall structural change involves the insertion of a single
carbon atom between the two of the original double bond.

Scheme 8
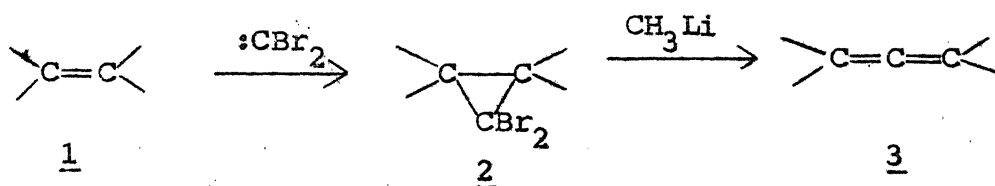
All the allenes synthesized showed properties in agreement with those in the literature.[19-23] The purity of each allene was checked by GLC before use. Dihydroboration of allenes was achieved using a standard solution of borane in tetrahydrofuran.[3] There was obtained a white precipitate in each case on allowing the reaction mixture to stir for sufficient time (12-14 hr). The resulting organoboranes were treated with alkaline hydrogen peroxide and worked up in the usual manner. The mixture of products was carefully analyzed by TLC and then subjected to column chromatographic separation. The identity of the products was established by comparison of GLC retention times and IR with those of authentic samples or by elemental analysis and spectral evidences.

III.3.1 Dihydroboration of 1,2-Cyclotridecadiene (4)

The products formed from the dihydroboration of 1,2-cyclotridecadiene (4) in tetrahydofuran (1:1.3 mol ratio of allene: borane) followed by alkaline hydrogen peroxide oxidation gave 5% of a mixture of hydrocarbons containing cis-cyclotridecene (5), trans-cyclotridecene (6) and bicyclo(10.1.0)tridecane (7) in the ratio 1:7:2, 1.5% cyclotridecanone (8), 27% cyclotridecanol (9), 14% cis-1,2-cyclotridecane diol (10), 15% trans-1,2-cyclotridecane diol (11) and 3.5% of a mixture of isomeric diols which has been tentatively assigned as a mixture of cis- and trans-1,3-cyclotridecane diol (12) as shown in the Scheme 9. All the products except 12 were identified unambiguously using authentic samples.

However, dihydroboration of 1,2-cyclotridecadiene (<u>4</u>) with borane followed by hydrolysis with sodium hydroxide at 80° for 24 hr and oxidation with alkaline hydrogen peroxide at 0° afforded 7% of a mixture of cis-cyclotridecene (<u>5</u>) and trans-cyclotridecene (<u>6</u>) in the ratio 17:83 and 60% of cyclotrideca-nol (<u>9</u>) (Scheme 10).

<p align="center">Scheme 10</p>
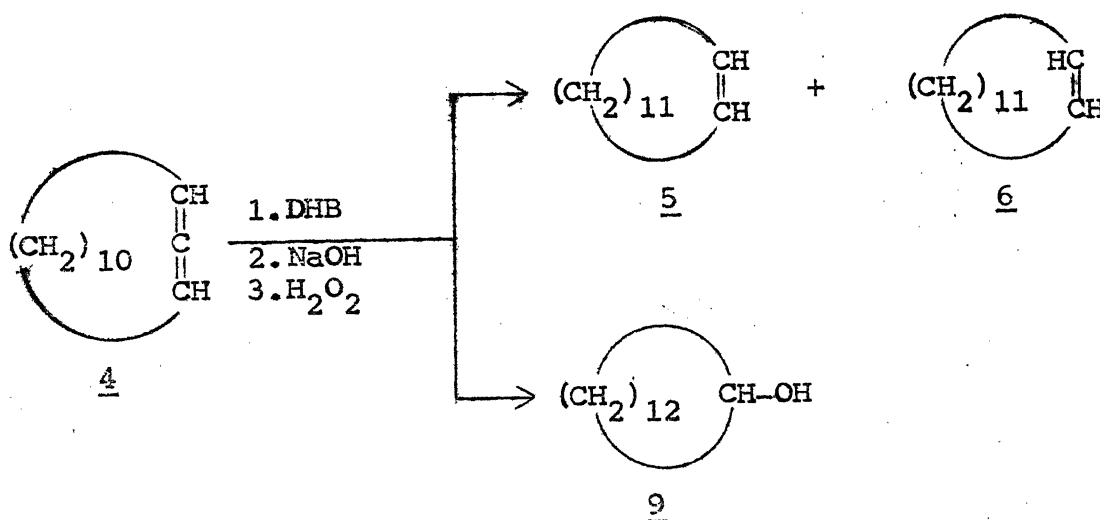
On the other hand dihydroboration-oxidation with chromium trioxide-pyridine yielded 50% of a mixture of cis-cyclotridecene (<u>5</u>) and trans-cyclotridecene (<u>6</u>) in the ratio 3:17 and 3% of cyclotridecanone (<u>8</u>) (Scheme 11). The results on the dihydro-boration of <u>4</u> are summarized in the Table 1.

<p align="center">Scheme 11</p>
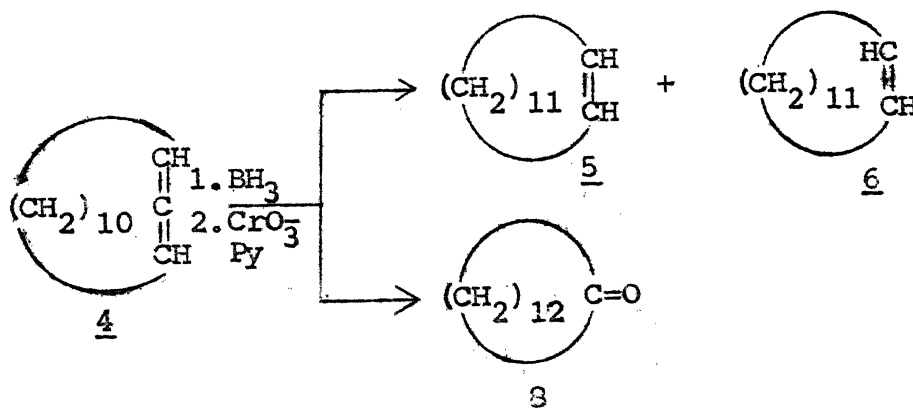
Table 1

Dihydroboration of 1,2-Cyclotridecadiene (4)

Products	% Yield		
	DHB-H$_2$O$_2$-NaOH	DHB-NaOH-H$_2$O$_2$	DHB-CrO$_3$
cis-Cyclotridecene (5)	5	7	50
trans-Cyclotridecene (6)	(5+6+7)	(5+6)	(5+6)
Bicyclo(10.1.0)tri-decane (7)	–	–	–
Cyclotridecanone (8)	1.5	–	3
Cyclotridecanol (9)	27	60	–
cis-1,2-Cyclotri-decane diol (10)	14	–	–
trans-1,2-Cyclotri-decane diol (11)	15	–	–
1,3-Cyclotridecane diol (12)	3.5	–	–

III.3.2 Dihydroboration of 1,2-Cyclononadiene (13)

1,2-Cyclononadiene (13) on dihydroboration-oxidation provided 0.6% trans-cyclononene (14), 0.3% cyclononanone (15) 31% cyclononanol (16), 11% cis-1,2-cyclononane diol (17),11% trans-1,2-cyclononane diol (18) and 0.8% trans-1,3-cyclononane diol (19) as shown in Scheme 12. All the products were identified by comparison with authentic samples.

Scheme 12
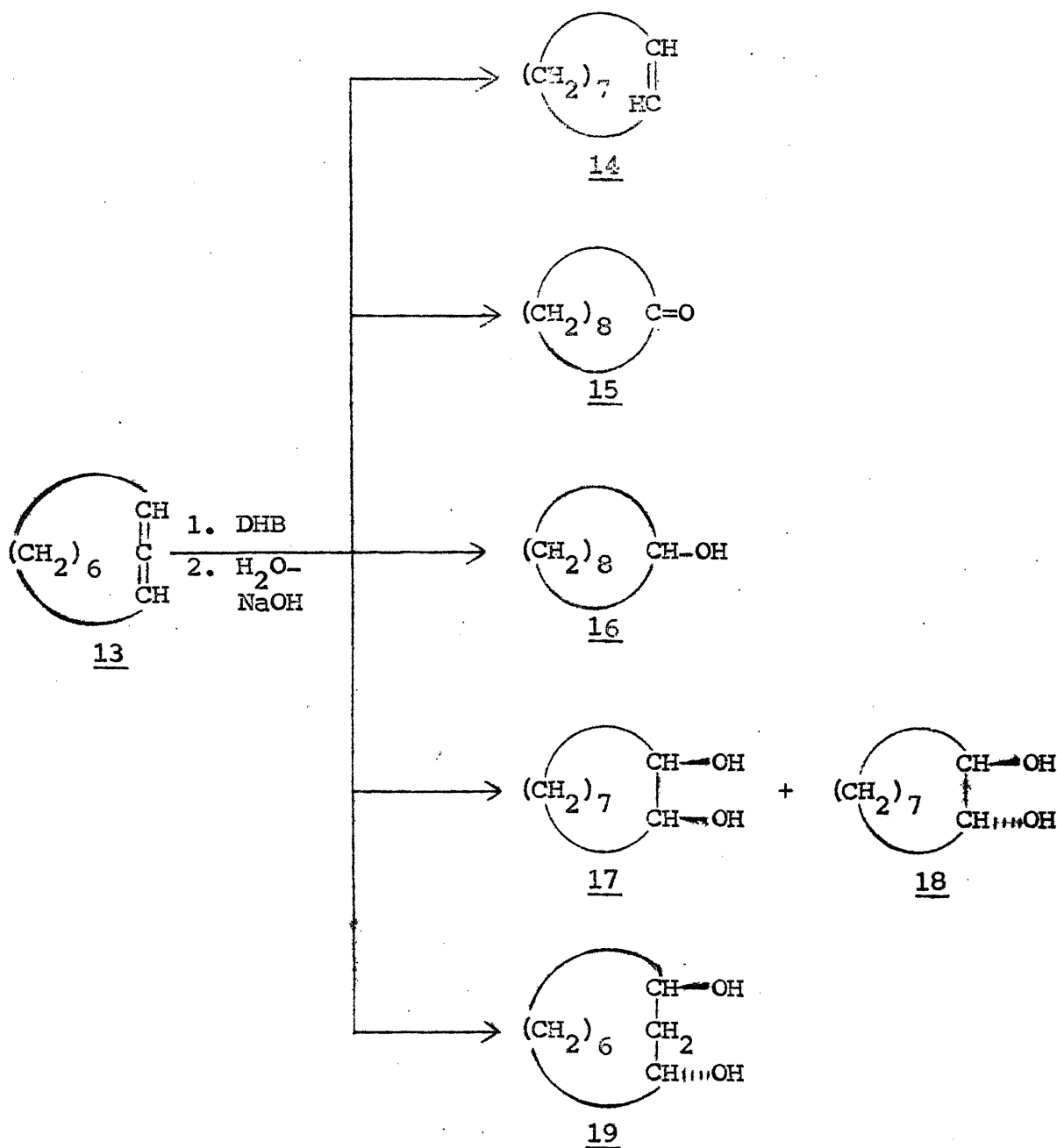
III.3.3 Dihydroboration of 3-Ethyl-1,2-pentadiene (20)

The organoboranes obtained by dihydroboration of 3-ethyl-
1,2-pentadiene (20) on oxidation with alkaline hydrogen peroxide

afforded 7% 3-ethyl-2-pentanol (21) and 40% 3-ethyl-1,2-pentane diol (22) (Scheme 13). Structures of 21 and 22 were confirmed by elemental analysis, IR and NMR. The NMR spectrum of 21 displayed signals at δ 3.9 (m, 1H) due to hydroxyl bearing methine proton and 0.9-1.5 (m, 15H). 3-Ethyl-1,2-pentane diol (22) had NMR bands at δ 3.5-3.9 (m, 3H) attributed to hydroxyl group bearing methine and methylene protons, 3.0 (s, 2H) due to hydroxyl protons and 1.0-1.4 (m, 11H).

Scheme 13
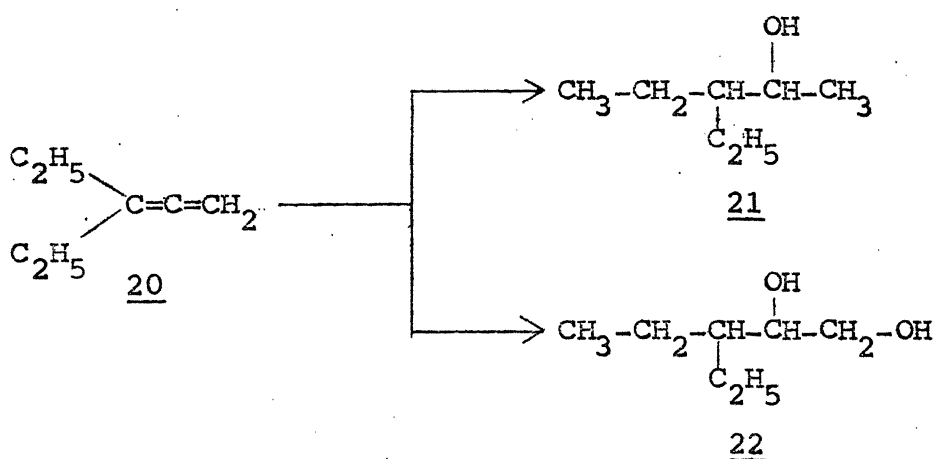
III.3.4 Dihydroboration of 3-Phenyl-1,2-butadiene (23)

·Treatment of 3-phenyl-1,2-butadiene (23) with excess of borane in tetrahydrofuran followed by hydrolysis and oxidation with hydrogen peroxide produced a mixture of products which on column chromatographic separation gave 11% 3-phenyl-2-butanol (24), 7% 3-phenyl-1-butanol (25), 8% 3-phenyl-1,3-butane diol (26), and 60% 3-phenyl-1,2-butane diol (27) (Scheme 14). The identity of the products was based on elemental analysis, IR

and NMR.

Scheme 14
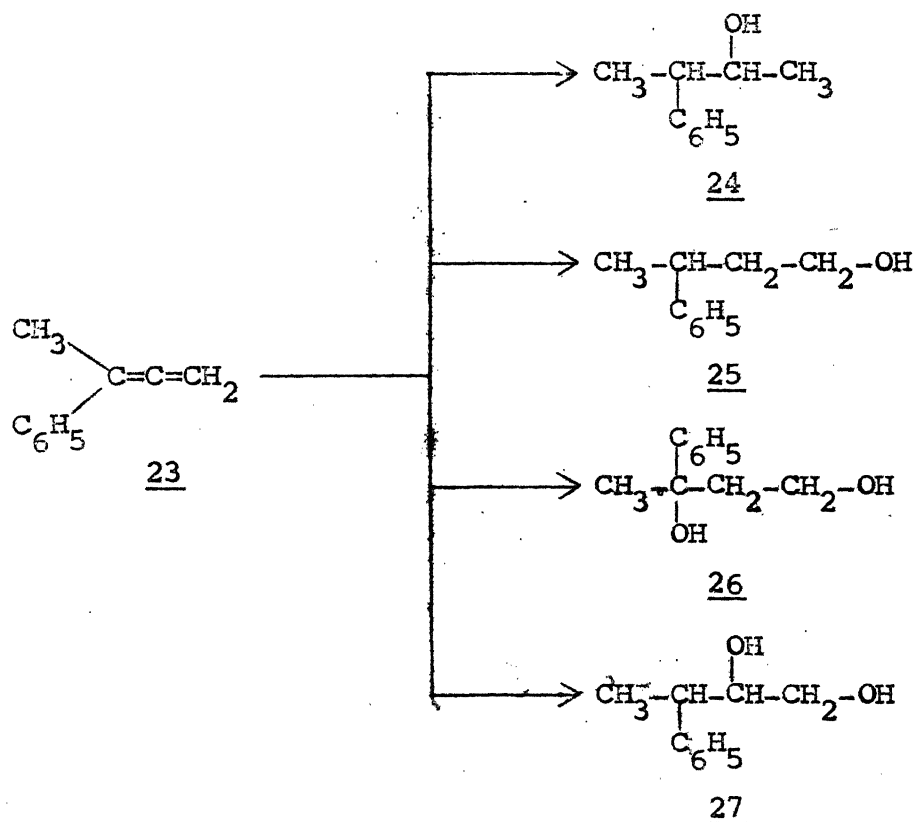
The NMR spectrum of 24 showed bands at δ 7.3 (s, 5H) aromatic protons, 3.8 (q, J = 6 Hz, 1H) hydroxyl bearing methine proton 2.82 (q, J = 7 Hz, 1H) benzilic proton, 1.75 (s, 1H) hydroxyl proton, 1.3 (d, J = 7 Hz, 3H) methyl protons and 1.0 (d, J = 6 Hz, 3H) methyl protons. The NMR of 25 displayed bands at δ 7.5 (s, 5H) aromatic protons, 3.5 (t, J = 6 Hz, 2H) hydroxyl bearing methylene protons, 2.62 (q, J = 7 Hz, 1H) benzylic proton, 1.84 (t, J = 6 Hz, 2H), methylene protons 1.75 (s, 1H) hydroxyl and 1.35 (d, J = 7 Hz, 3H) methyl protons. 26

and 27 had NMR spectra expected of their structures.

III.3.5 Dihydroboration of Phenylpropadiene (28)

The dihydroboration and oxidation of phenylpropadiene (28) proceeded to give 2.5% 1-phenyl-1-propanol (29), 7.5% 1-phenyl-2-propanol (30), 5% 3-phenyl-1-propanol (31) and 38% 1,3-propane diol (32) (Scheme 15). The identity of all the products was established by comparison of GLC retention times and IR spectra with those of authentic samples (Scheme 15).

Scheme 15

$$C_6H_5-CH=C=CH_2 \xrightarrow[Ox.]{DHB}$$
28

$$\longrightarrow C_6H_5-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$$
29

$$\longrightarrow C_6H_5-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$$
30

$$\longrightarrow C_6H_5-CH_2-CH_2-CH_2-OH$$
31

$$\longrightarrow C_6H_5-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2OH$$
32
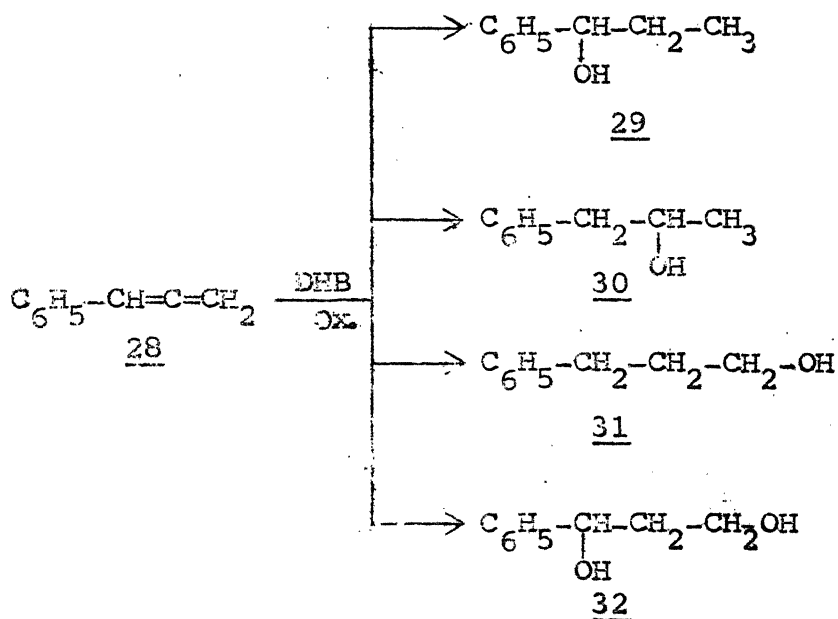
III.3.6 Dihydroboration of Acetylenes

The gem- and vic-organoboranes have been obtained from the dihydroboration of acetylenes. The dihydroboration of acetylenes followed by basic hydrogen peroxide oxidation has been extensively studied by several group of workers.[3,13-16]

Logan and Flautt[13] isolated 2,2,5,5-tetramethyl-3-hexanol (34)
and 2,2,5,5-tetramethyl-3,4-hexane diol (35) from dihydrobora-
tion of di-t-butylacetylene (33) (Scheme 16). These authors
rationalized the formation of the monoalcohol as possibly
occurring by reduction of the corresponding carbonyl compound,
formed by hydrolysis and oxidation, by some reducing species (BH)
present in the mixture during work-up.

<div align="center">Scheme 16</div>

$$t-C_4H_9-C\equiv C-C_4H_9-t \xrightarrow{\text{DHB}}
\begin{cases}
t-C_4H_9-CH_2-\underset{\underset{OH}{|}}{CH}-C_4H_9-t & \mathbf{34} \\
\\
t-C_4H_9-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-C_4H_9-t & \mathbf{35}
\end{cases}$$

$$\mathbf{33}$$
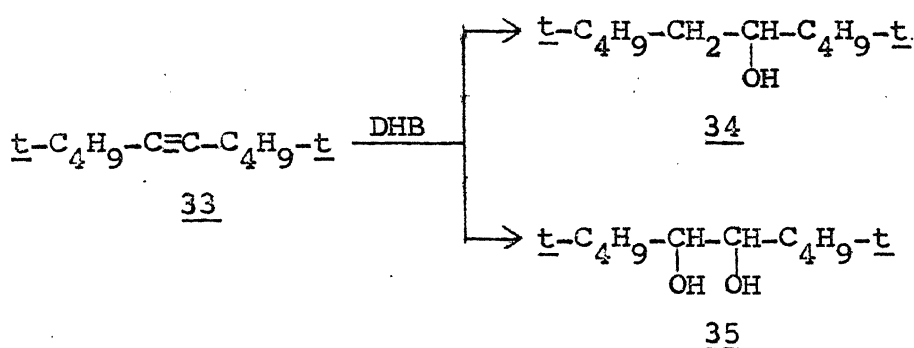
Brown and Zweifel[3] isolated 1-hexanal (37), 1-hexanol
(38) and 1,2-hexane diol (39) from the dihydroboration of
1-hexyne (36); 3-hexanone (41), 3-hexanol (42) and 3,4-
hexane diol (43) from 3-hexyne (40). From evidences gathered
from the dihydroboration of 1-hexyne (36), the authors visualized
the formation of 3-hexanol (42) as occurring via a base-catalyzed
hydrolysis of gem-diboro-organoborane (44) to monoboro-organo-
borane (45) followed by oxidation (Scheme 17).

Scheme 17

$$CH_3-(CH_2)_3C \equiv CH \xrightarrow{\hspace{2cm}}$$

36

$$\longrightarrow CH_3-(CH_2)_4-CHO$$

37

$$\longrightarrow CH_3-(CH_2)_4-CH_2-OH$$

38

$$\longrightarrow CH_3-(CH_2)_3-\underset{\underset{OH}{|}}{CH}-CH_2-OH$$

39

$$CH_3-CH_2-C \equiv C-CH_2-CH_3 \xrightarrow{\hspace{2cm}}$$

40

$$\longrightarrow CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

41

$$\longrightarrow CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_3$$

42

$$\longrightarrow CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$$

43

$$CH_3-CH_2-\overset{\overset{\diagdown \diagup}{\underset{|}{B}}}{\underset{\underset{B}{|}}{C}}-C_3H_7-n \xrightarrow{\overset{\ominus OH}{H_2O}} CH_3-CH_2-\underset{\underset{\diagdown \diagup}{\underset{B}{|}}}{CH}-C_3H_7-n \longrightarrow 42$$

44 $\hspace{5cm}$ 45
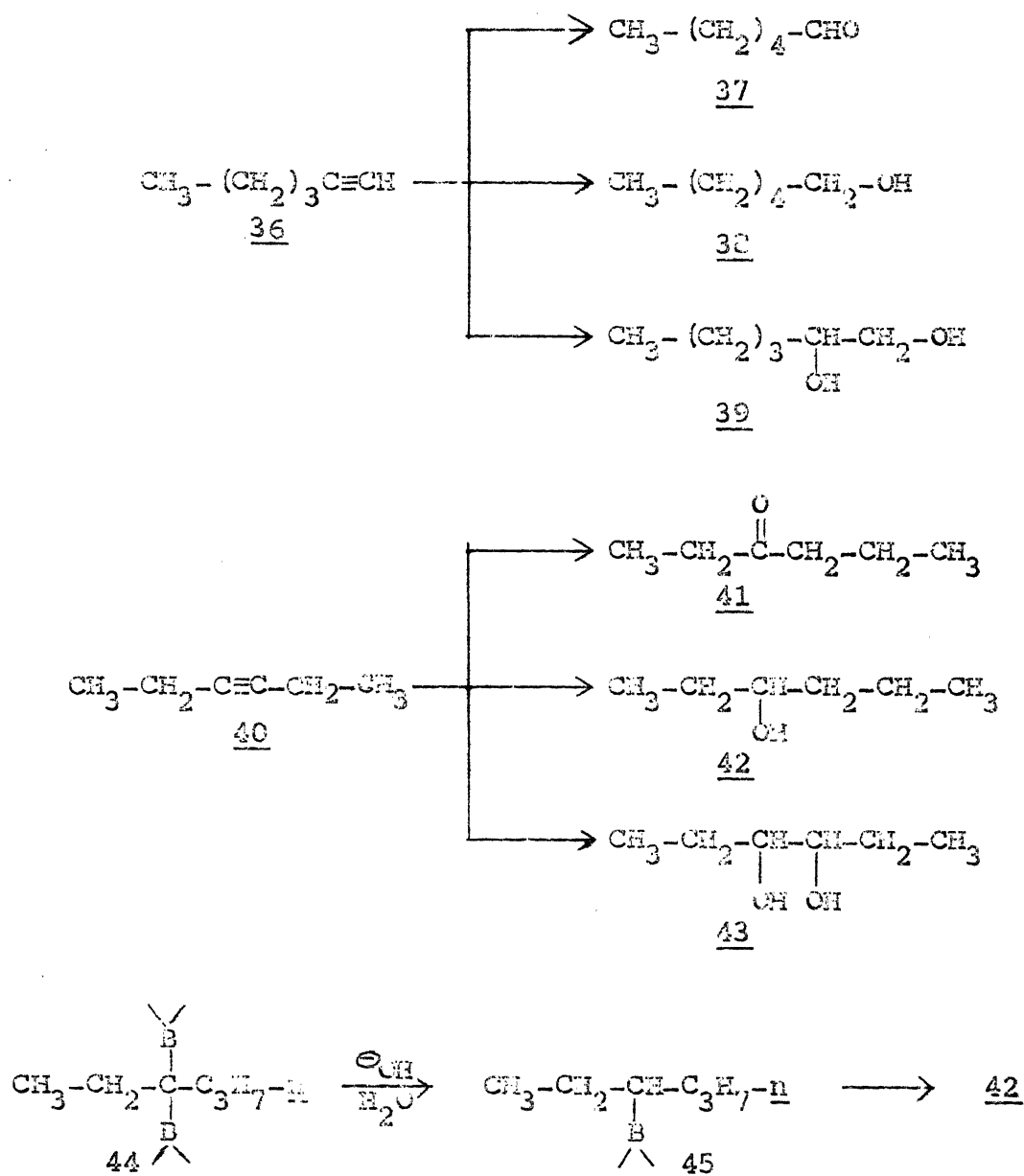
Hassner and Braun[14] isolated trans-stilbene (47), deoxy-
benzoin (48), 1,2-diphenylethanol (49) and dl-hydrobenzoin (50)
from dihydroboration of diphenyl acetylene (46). The formation

of <u>trans</u>-stilbene (<u>47</u>) was postulated as occurring by the elimination of boron-boron bonded species from <u>vic</u>-diboro organoborane (<u>51</u>) as shown in Scheme 18.

<div align="center">Scheme 18</div>
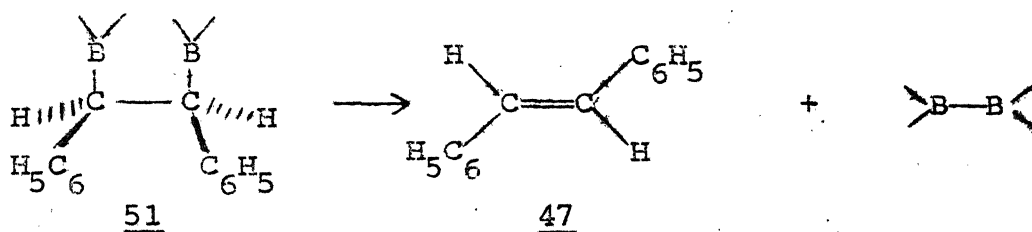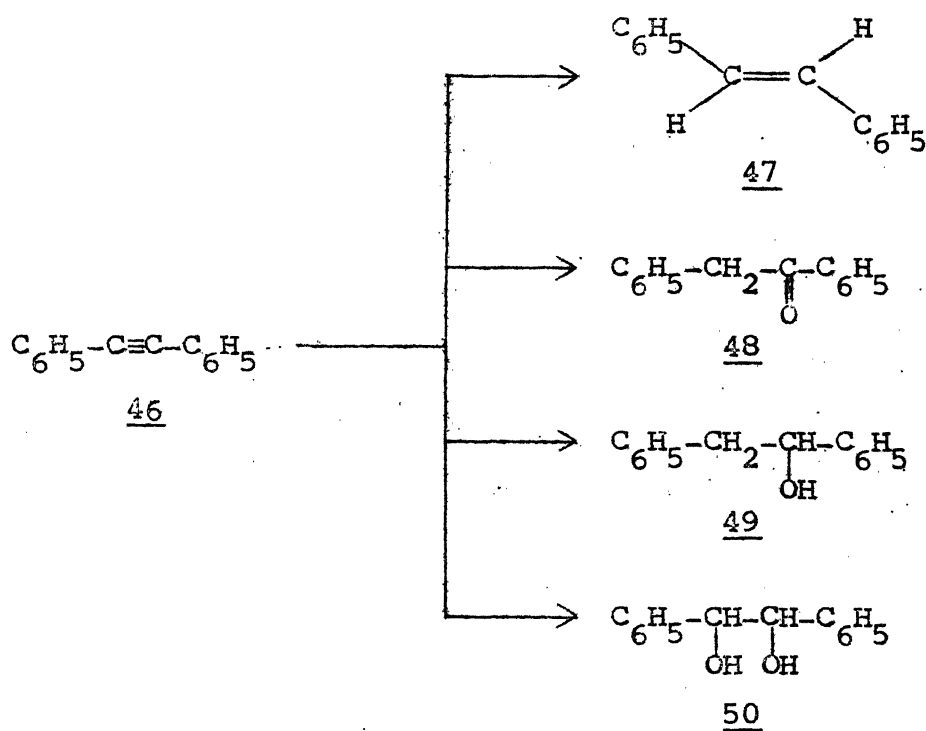
However, the proposed mechanism by Hassner and Braun[14] was in direct contradiction with the mechanism of Pasto and Miesel[24,25] for such an elimination or transfer reaction.

According to Pasto and Miesal the β-substituent to the boron
atom must possess a non-bonded electron pair capable of complex-
ing with boron to initiate the reaction relieving the instability,
and the stereochemistry must be such as to allow intramolecular
complexing to occur. In this case the β-boron has no non-bonded
pair of electrons, and therefore, 51 is expected to be stable
towards such elimination reaction. In addition, the reverse of
this postulated elimination is known to occur.

Hassner and Braun[14] also suggested a possible mechanism
for the formation of monoalcohol (49) via hydroboration of a
postulated intermediate (53) formed by an intramolecular hydride
shift in vinyl organoborane (52); followed by oxidation (Scheme 19).

<u>Scheme 19</u>

$$C_6H_5-C\equiv C-C_6H_5 \xrightarrow{BH_3}$$

46

52

$$C_6H_5-CH_2-\overset{C_6H_5}{\underset{}{C}}=B- \xrightarrow{BH_3} C_6H_5-CH_2-\underset{}{CH}-C_6H_5$$

53

54

$$\xrightarrow{[O]} C_6H_5-CH_2-\underset{OH}{CH}-C_6H_5$$

49
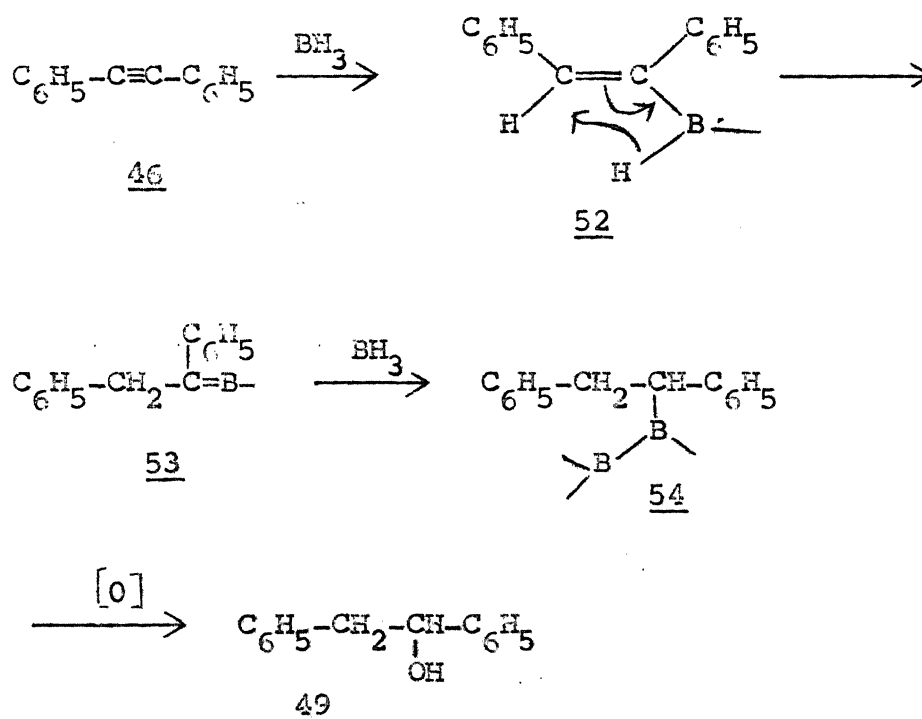
At this stage Pasto[15] did a detailed study on the dihydro-
boration of diphenylacetylene (46) and isolated a small amount
of cis-stilbene and dibenzyl along with the mixture of products
as reported by Hassner and Braun.[14] The deuterium labelling
studies have indicated that many of the previously suggested
mechanisms are not operative and that the vic-diboro organo-
borane (51) is the precursor for olefin (47), monoalcohol (49)
and 1,2-diol (50) in the case of internal acetylenes. The
labelling experiments have indicated that the vic-diboro organo-
borane (51) undergoes exceedingly rapid base-catalyzed hydrolysis
indicating participation by neighbouring boron during hydrolysis.
The proposed bridged boron anion (55) may undergo elimination to
give trans-stilbene (47); deuterolysis to give monoboro organo-
borane (58) which on oxidation gives β-deuterioalcohol (59)
(Scheme 20).

<div align="center">Scheme 20</div>
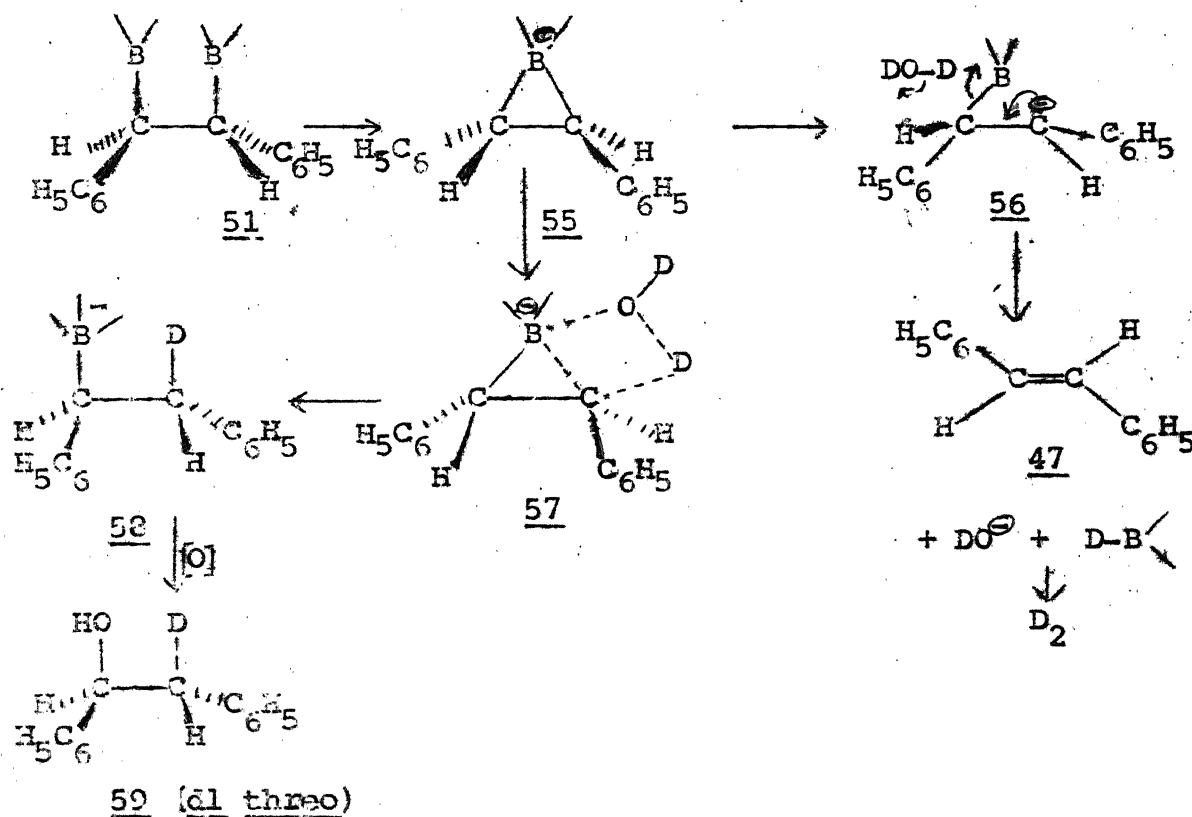
The inability to detect olefin (47) prior to deuterolysis and detection of cis-stilbene were not compatible with an elimination of a boron-boron bonded species. The stereochemistry of the intermediate vic-diboro organoborane (51) formed by two cis-additions of $>$B-H to carbon-carbon triple bond would require the formation of trans-stilbene (47) from diphenyl acetylene (46). The possibility for the formation of olefin by the hydrolysis of a vinylic carbon-boron bond has been eliminated by the lack of deuterium incorporation in the olefin during deuterolysis.

The monoalcohol (49) was shown not to be formed exclusively by hydrolysis of the gem-diboro organoborane (61) followed by oxidation as suggested by Brown and Zweifel[3] or by hydroboration of the intermediate organoborane (53) having a carbon-boron double bond[14] or by reduction of an intermediate carbonyl compound (4) during work-up as evidenced by the incorporation of deuterium both in positions 1 and 2 of 1,2-diphenylethanol (50) obtained from diphenylacetylene (46). Furthermore, the rate of incorporation of deuterium in 2-position of monoalcohol (49) occurred at a rate comparable to the rate of incorporation of deuterium at 1-position, and the rates were considerably faster than the deuterolysis of monoboro organoborane. The enhanced rate of deuterolysis of carbon-boron bond of the vic-diboro organoborane (51) has been explained by invoking the participation by the neighbouring boron in two ways during

carbanion formation as the _trans-stilbene_ (<u>47</u>) is formed in great excess over the _cis_-isomer. It would appear that the anion (<u>55</u>) with retention in configuration is preferred over the anion (<u>60</u>) with inversion (Scheme 21). As expected, the anion (<u>55</u>) with retention in configuration would give the desired dl-threo monoalcohol (<u>59</u>) and by direct elimination the desired _trans-stilbene_ (<u>47</u>) on deuterolysis (Scheme 20).

<u>Scheme 21</u>

(Retention)

<u>51</u>   <u>55</u>

(Inversion)

<u>51</u>   <u>60</u>
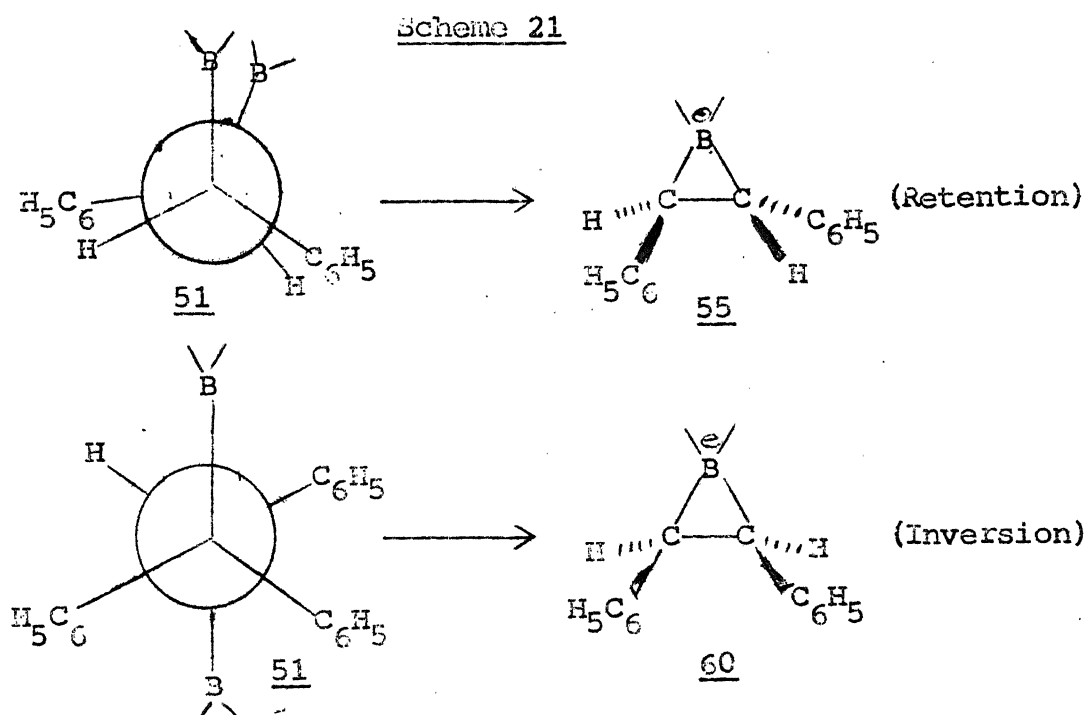
The formation of monoalcohol (<u>63</u>) with deuterium incorporated at 1-position and deoxybenzoin (<u>48</u>) has been indicated from gem-diboro organoborane (<u>61</u>) (Scheme 22).

<u>Scheme 22</u>

$C_6H_5-CH_2-CD-C_6H_5$ <u>62</u> $\xrightarrow{[O]}$ $C_6H_5-CH_2-\overset{OH}{\underset{}{CD}}-C_6H_5$ <u>63</u>

$C_6H_5-CH_2-\overset{}{\underset{}{C}}-C_6H_5$

$C_6H_5-CH_2-\overset{}{\underset{O}{C}}-C_6H_5$ <u>48</u>
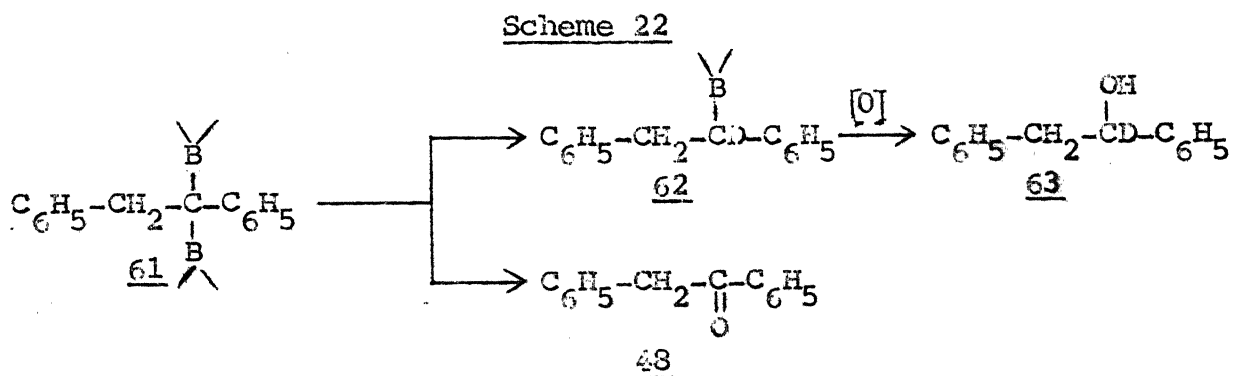
All these facts, in short, point out that dihydroboration of acetylenes depends upon the structure of the acetylene. An internal acetylene gives vic-diboro organoborane as the major product, whereas gem-diboro organoborane is obtained as the major product from terminal acetylenes.

III.3.8 Dihydroboration of Allenes

In principle, two successive cis-additions of boron-hydrogen bond to two orthogonal double bonds of an allene (3) could give rise to gem-, vic- and 1,3-diboro organoboranes (66, 67 and 68) via vinyl and allyl organoboranes (64 and 65) as shown in the Scheme 23.

<u>Scheme 23</u>
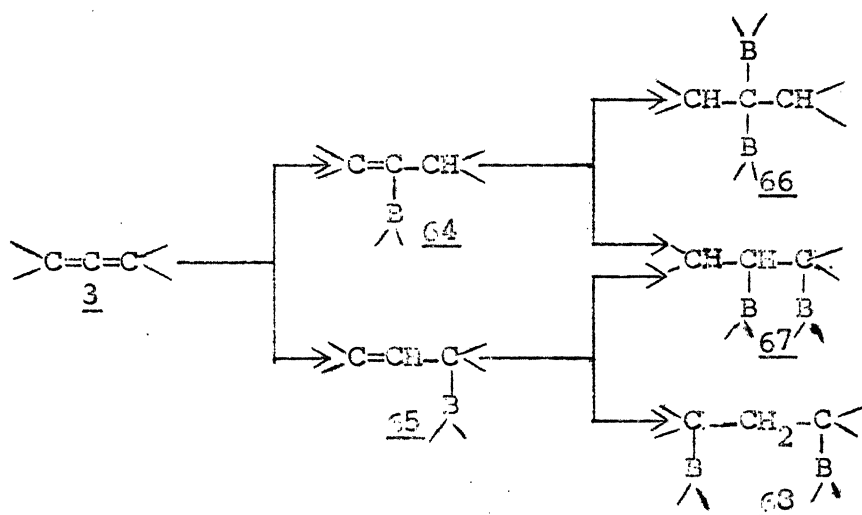
The monohydroboration of cyclic as well as acyclic allenes is well precedented in the literature.[1,2,4,5] It has been shown that cyclic and 1,3-disubstituted acyclic allenes (69 and 71) undergo monohydroboration to give vinyl organoboranes (70 and 72)

as the major products, while mono- and 1,1-disubstituted allenes
(73 and 74) provide mainly allyl organoborane (75) by attack of
the boron at the least hindered terminal carbon atom of the
allenic linkage (Scheme 24).

Scheme 24

69 → 70A (cis); 70B (trans)

$R-CH=C=CH-R$ ⟶ $R-CH=C-CH_2-R$

71 → 72

75
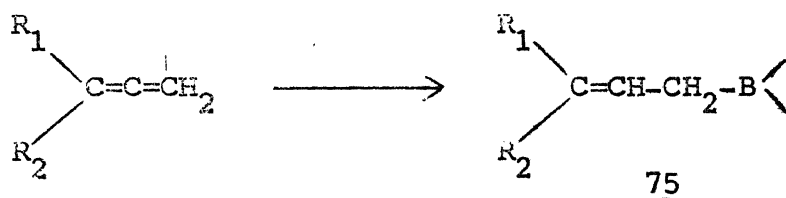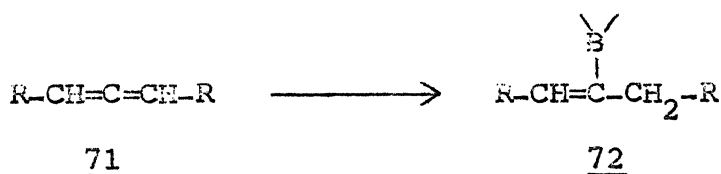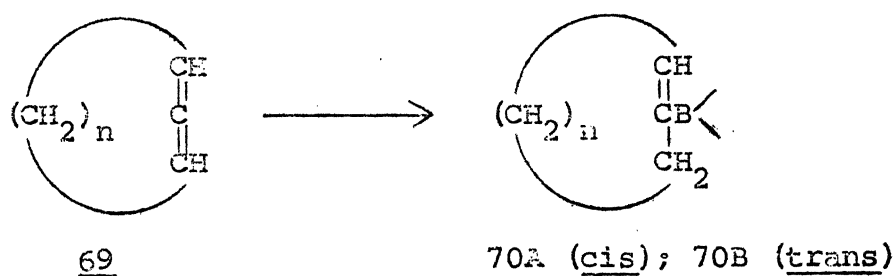
73 (R_1 = H; R_2 = alkyl);
74 (R_1 = R_2 = allyl).

In the case of cyclic allenes the formation of vinyl
organoborane (70) is directed by the ring size which   forces
the boron-hydrogen of borane or any other hydroborating species
to approach from the ring side or hydrogen side. However, the
attack from the hydrogen side is preferred for steric reason.

Based on the dihydroboration study of diphenyl acetylene (46) it
is reasonable to assume the second boron-hydrogen bond cis-
addition would lead mainly to the formation of 1,2-diboro organo-
borane (76A) with threo configuration. However, the formation
erythro -vic-diboro organoborane (76B) from trans-vinyl organo-
borane (70B) is also possible to some extent. Now the trans-
olefin (78A) as the only product or the major product can be
visualized via the anion (77A) by direct elimination. Similarly,
the minor cis-olefin (78B) can arise from the anion (77B)
(Scheme 25) in accordance with Pasto's mechanism.[15] The exclusive
path for the formation of the anion 77A seems to be from the
vic-diboro organoborane 76A.

Scheme 25

76A (threo)   70A (cis)   70B (trans)   76B (erythro)

inversion

retention   retention

77A   73A   78B   77B
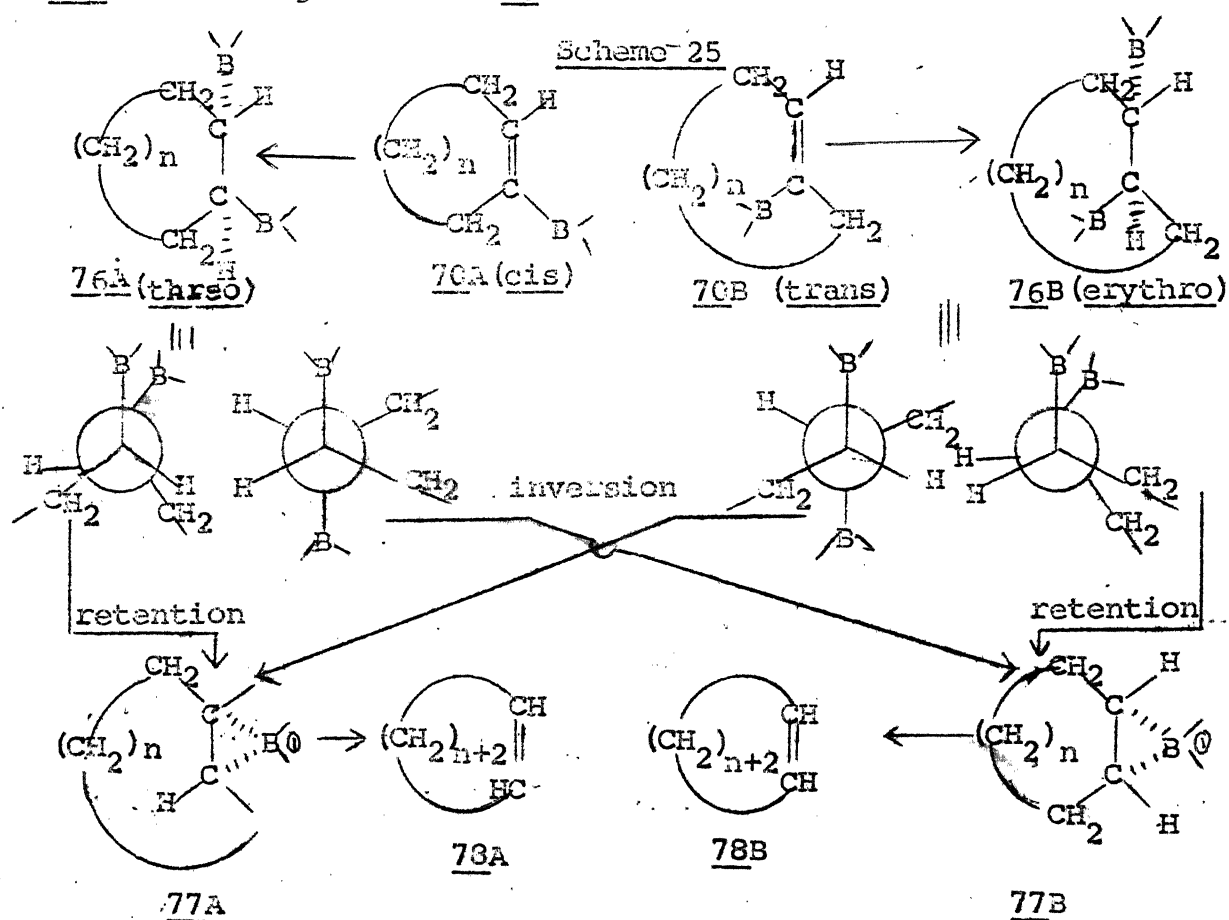
It has been established that the terminal carbon attack by boron increases from 1,2-cyclononadiene (13) to 1,2-cyclotridecadiene[5] (4). So, we suggest that the formation of the interesting bicyclo(10.1.0)tridecane (7) from 4 is possibly occurring from 1,3-diboro organoborane (79) via the bridged anion (80) as shown in the Scheme 26.

Scheme 26
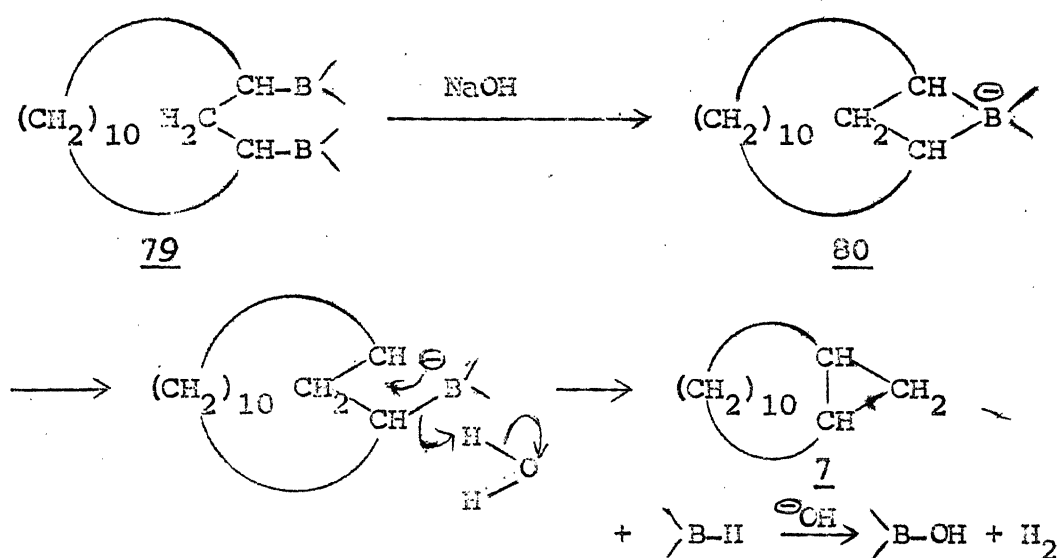
There are three possible routes for the genesis of the monoalcohol (84) (Scheme 27). The dihydroboration study on diphenyl acetylene (46) suggests that the monoalcohol (84) is exclusively by hydrolysis of the vic-diboro organoborane (76) followed by oxidation. The observed increase in the amount of cyclotridecanol (9) formed when the time of hydrolysis was enhanced, is in agreement with Pasto's observation[15] that

Scheme 27
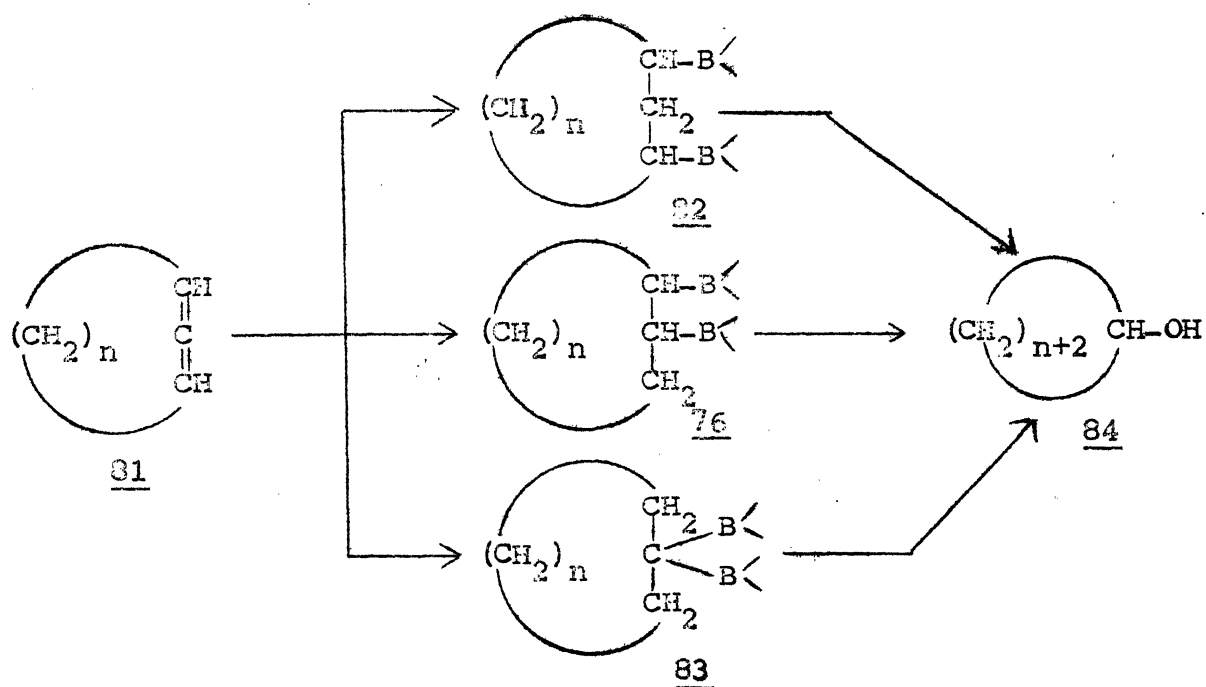
vic-diboro organoborane (76) undergoes hydrolysis faster than the monoboro organoborane. The formation of the cyclic ketone is visualized via 83, whereas 76 and 82 can give rise to isomeric 1,2- and 1,3-diols respectively.

Brown and coworkers[3] have shown that organoboranes can be converted to the corresponding ketones by chromic acid oxidation. In view of this, an attempt was made to find the relative amounts of various organoborane intermediates in the dihydroboration of 1,2-cyclotridecadiene (4). To our surprise chromium trioxide-pyridine oxidation of the organoboranes gave mainly olefinic products in high yield (Scheme 11). The formation of the olefinic products (5 and 6) can be explained via a two-step path or/and

one-step path as shown in the Scheme 28.

Scheme 28

$$O{=}Cr\diagup_{O{-}B\diagdown}^{O{-}B\diagup} \quad + \quad (CH_2)_{11}\underset{HC}{\overset{CH}{\|}} \quad \underline{6}$$
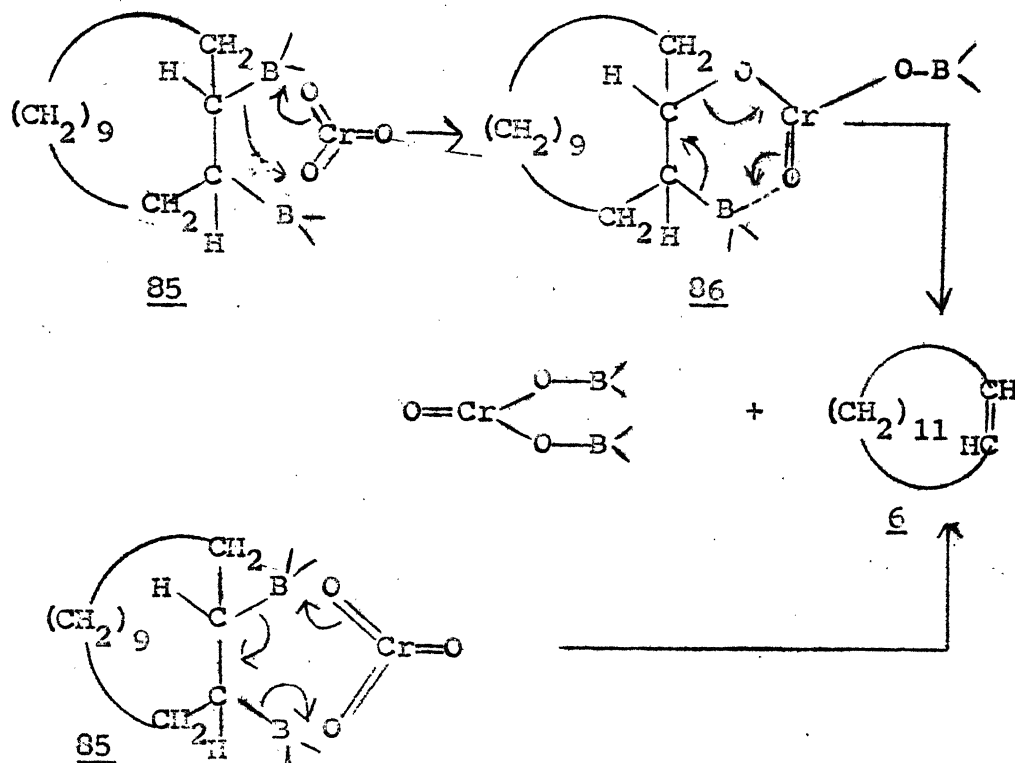
3-Ethyl-1,2-pentadiene (20) gave 40% of 3-ethyl-1,2-pentane diol (22) and 7% of 3-ethyl-2-pentanol (21). The result can be explained via 1,2-diboro organoborane (86) (Scheme 29).

Scheme 29
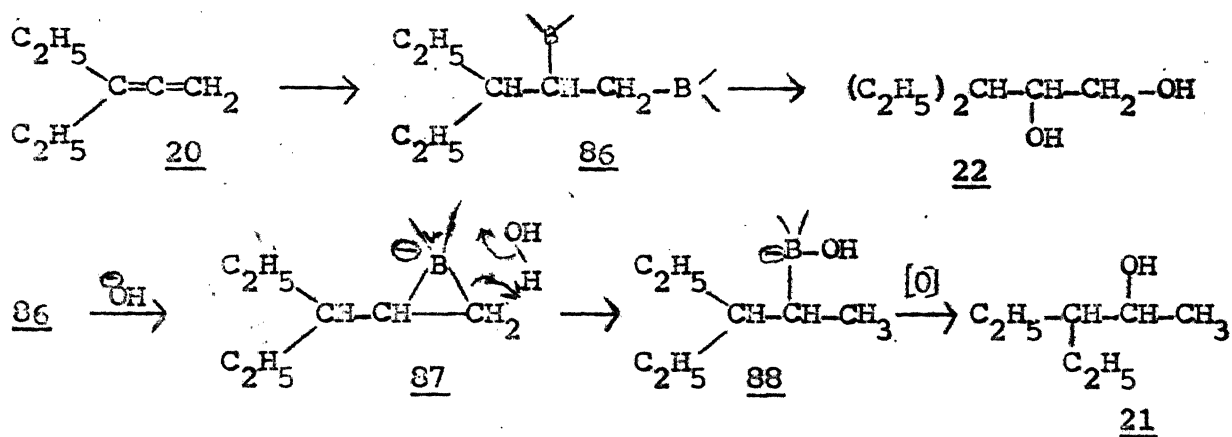
The formation of 3-ethyl-2-pentanol (21) as the only monoalcohol
further substantiates the presence of a cyclic boron anion (87)
from 86. The water approaches only from the least hindered side
to form the more substituted alcohol, 3-ethyl-2-pentanol (21)
after oxidation. At present we have no explanation to offer for
the absence of olefinic products in the dihydroboration of 20.

3-Phenyl-1,2-butadiene (23) behaves almost like 3-ethyl-
1,2-pentadiene (20) except that a small amount of 1,3-diboro-
organoborane is also formed in addition to 1,2-diboro organo-
borane. In the case of phenylpropadiene (28), the formation of
1-phenyl-1,3-propane diol (32) is in accordance with that reported
by Carsano.[6] Our results suggest that the second $>$B-H addition
to the initially formed allyl organoborane (89) (Scheme 30) is

<u>Scheme 30</u>

$$C_6H_5-CH=C=CH_2 \xrightarrow{\quad >B-H \quad} C_6H_5-CH=CH-CH_2-B< \xrightarrow{\quad >B-H \quad}$$

28   89

$$C_6H_5-\overset{\overset{\displaystyle \backslash \, /}{\underset{|}{B}}}{C}H-CH_2-CH_2-B< \longrightarrow C_6H_5-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-CH_2-OH$$

90   32
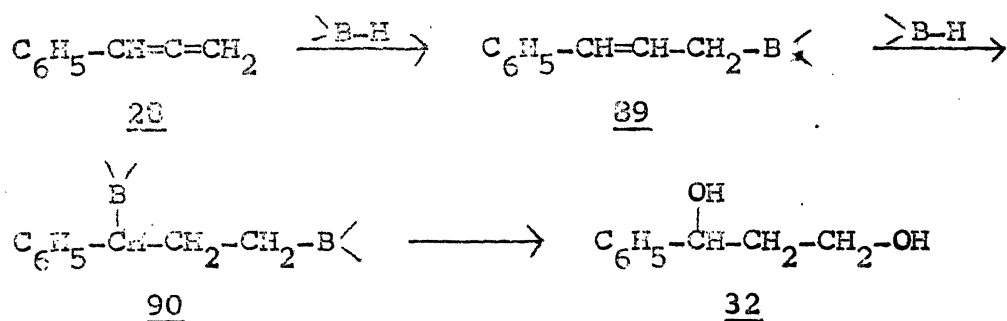
dictated mainly by the steric effects caused by a phenyl group
on one side and a boromethyl group on the other side, and also
by the electronic effect of the phenyl group to some extent.
The predominant formation of 32 indicates that the second boron

attack is favoured at the methine carbon bearing the phenyl group to form 1,3-diboro organoborane (90). The formation of the monoalcohols (29 - 31) may be visualized from the possible gem-,vic- and 1,3-dibora organoborane intermediates as discussed before.

III.4 EXPERIMENTAL

Boiling points are uncorrected. Melting points were taken in open capillaries using Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 700 or 137B spectrophotometer using potassium bromide discs or as liquid films between sodium chloride plates. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Associates A-60 NMR spectrophotometer in deuterated chloroform with tetramethylsilane as the internal standard. Gas liquid chromatographic (GLC) analyses were made with Aerograph Model 9C-P instrument using 10 ft carbowax column. Silica gel (ASW) or basic alumina (E. Merck) was used for thin layer chromatography (TLC). Column chromatography was done on basic alumina columns. Microanalyses were done by Mr.A.H.Siddiqui, Microanalyst of the Department of Chemistry, Indian Institute of Technology, Kanpur-16, India.

Starting Materials

1,2-Cyclononadiene was synthesized as described in Chapter I.4. Cyclododecene (Columbia), 2-ethyl-1-butene

(Aldrich Co.), styrene (BDH) and α-methylstyrene (BDH) were used as such. Chromium trioxide (BDH) was stored in a vacuum desiccator over phosphorous pentoxide prior to use. Sodium dichromate was used as such. Analytical grade pyridine (BDH) was used without further purification. Other materials used were the same as described in Chapter I.4.

Preparation of 13,13-Dibromobicyclo(10.1.0)tridecane

From cyclododecene (42 g, 0.25 mol), potassium (10 g, 0.25 g atom), bromoform (63 g, 0.25 mol) and 300 ml of dry t-butanol, there was obtained 59 g (70%) of 13,13-dibromobicyclo-(10.1.0)tridecane, bp 100-102° at 0.02 mm , n_D^{25} 1.5433 (lit[20], bp 110-115° at 0.08 mm).

The compound was found to be saturated to neutral potassium permanganate and bromine. GLC on a 2 ft silicone rubber column indicated it to be a single compound.

Preparation of 1,2-Cyclotridecadiene

13,13-Dibromobicyclo(10.1.0)tridecane (70 g, 0.20 mol) was treated with methyllithium prepared from lithium (5.6 g, 0.80 g atom) and methyl iodide (56.8 g, 0.040 mol) at -40 to -45° to give 23.4 g (80%) of 1,2-cyclotridecadiene, bp 74-76° at 0.4 mm , n_D^{27} 1.5050 (lit[20], bp 83-85° at 3 mm).

The IR spectrum of the compound showed medium-strong band at 1950 cm^{-1} characteristic of the allenic linkage. GLC indicated it to be a single substance. NMR showed a band at δ 4.94 (m, 2H) in agreement with its structure.

Preparation of 1,1-Dibromo-2,2-diethylcyclopropane

From 2-ethyl-1-butene (33.6 g, 0.40 mol), potassium (10 g, 0.25 g atom), 300 ml of dry t-butanol and bromoform (63.3 g, 0.25 mol), there was obtained 39 g (61%) of 1,1-dibromo-2,2-diethylcyclopropane, bp 70° at 7 mm, n_D^{24} 1.5107 following the general procedure described in Chapter I.4.

The IR and qualitative chemical tests confirmed the absence of a double bond. The compound was found to be homogeneous by GLC.

Anal. for $C_7H_{12}Br_2$: Calcd: C, 32.80; H, 4.69.

Found: C, 33.01; H, 4.60.

Preparation of 3-Ethyl-1,2-pentadiene

1,1-Dibromo-2,2-diethylcyclopropane (39 g, 0.14 mol) was treated with methyllithium prepared from lithium (4.2 g, 0.60 g atom) and methyl iodide (42.6 g, 0.30 mol) at about-50° to give 7.2 g (53%) of 3-ethyl-1,2-pentadiene, bp 96° at 750 mm, n_D^{35} 1.4295 (Lit[22], bp 40-51° at 150 mm).

GLC analysis indicated it to be a single substance and IR showed characteristic allenic bands at 1950 and 850 cm^{-1}.

Preparation of 1,1-Dibromo-2-phenylcyclopropane

Alcohol free potassium t-butoxide (from 20 g, 0.50 g atom of potassium and 500 ml of dry t-butanol) was cooled to -20° and styrene (62.4 g, 0.60 mol) in 500 ml of pentane was added. Bromoform (151.8 g, 0.60 mol) was added over a period of 6 hr

and the usual extraction and fractionational distillation proce-
dure afforded 96 g (70%) of 1,1-dibromo-2-phenylcyclopropane,
bp 67-68° at 0.02 mm, n_D^{30} 1.5952 (lit.[19] bp 90-91° at 0.1 mm,
n_D^{22} 1.6001).

The purity of the compound was established by GLC. It
failed to react with bromine and neutral potassium permanganate.

Preparation of Phenylpropadiene

1,1-Dibromo-2-phenylcyclopropane (82.8 g, 0.30 mol) was
treated with methyllithium prepared from lithium (8.4 g, 1.2 g
atom) and methyl iodide (85.2 g, 0.60 mol) in dry ether at about
-60° to give 27 g (77%) of phenylpropadiene, bp 78° at 17 mm,
n_D^{28} 1.5794 (lit.[19] bp 64-65° at 11 mm, n_D^{24} 1.5809).

GLC analysis using a 10 ft carbowax column indicated it
to be pure. It showed strong IR absorptions at 1938 and 850 cm^{-1}
characteristic of allenes.

Preparation of 1,1-Dibromo-2-phenyl-2-methylcyclopropane

From α-methylstyrene (70.8 g, 0.60 mol), potassium
(20 g, 0.50 g atom), 500 ml of dry t-butanol and bromoform (151.8g,
0.60 mol), there was obtained 120 g (83%) of 1,1-dibromo-2-
phenyl-2-methylcyclopropane, bp 69-71° at 0.02 mm. The IR and
the usual qualitative tests showed the absence of olefinic double
bond in the compound.

Anal. for $C_{10}H_{16}Br_2$: Calcd: C, 41.40; H, 3.45.

Found: C, 41.72; H, 3.54.

Preparation of 3-Phenyl-1,2-butadiene

1,1-Dibromo-2-phenyl-2-methylcyclopropane (37 g, 0.30 mol) was treated with methyllithium prepared from lithium (8.4 g, 1.2 g atom) and methyl iodide (85.2 g, 0.60 mol) at -40 to -45° to yield 24 g (61%) of 3-phenyl-1,2-butadiene, bp 80-81° at 7 mm, n_D^{28} 1.5868 (lit.[21], bp 82° at 11 mm). The IR spectrum of the compound showed bands at 1940 and 850 cm^{-1} characteristic of the allenic group. The purity of the allene was checked by GLC.

Dihydroboration-Oxidation (Alkaline Hydrogen peroxide) of 1,2-Cyclotridecadiene

1,2-Cyclotridecadiene (3.56 g, 0.02 mol) in 40 ml of dry tetrahydrofuran was taken in a 500 ml three-necked flask equipped with a water condenser, pressure equilibrating dropping funnel, a low temperature thermometer and an inlet and outlet for dry nitrogen gas. The flask was immersed in ice-salt bath and 34 ml of 0.8M borane (0.08 hydride) was added through the dropping funnel over a period of 45 min at 0-5°. It was allowed to stir for 2 hr at 0-10° and for 20 hr at room temperature. The reaction mixture was then carefully hydrolyzed using 5 ml of water which gave 0.034 mol of unreacted hydride. Sodium hydroxide (1.2 g, 0.03 mol) dissolved in 6 ml of water was added to the mixture and allowed to stir for 15 min. During alkaline hydrolysis 80 ml of hydrogen was evolved. The mixture was subsequently oxidized using 20 ml of 30% hydrogen peroxide,

extracted with ether, washed with water and dried over anhydrous magnesium sulphate. Crude product (2.7 g) obtained after removal of the solvent showed 6 spots on a silica gel coated plate with chloroform-benzene (1:3). The material was chromatographed on a column prepared from a slurry of 160 g of basic alumina in petroleum ether (60-80°). Elution of the column with petroleum ether (60-80°) afforded 0.18 g (5%) of a liquid product. GLC analysis of the liquid product on a 10 ft carbowax column indicated it to be a mixture of cis-cyclotridecene, trans-cyclotridecene and bicyclo(10.1.0)tridecane in the ratio (1:7:2). These three components were separated by GLC and identified by comparison of GLC retention times and IR with authentic samples.

Anal. for $C_{13}H_{24}$: Calcd: C, 86.66; H, 13.33.

Found: C, 86.56; H, 13.44.

Further elution of the column with petroleum ether (60-80°) yielded 0.06 g (1.5%) of cyclotridecanone, 2,4-dinitrophenyl-hydrazone of which had mp and mixed mp 114° (lit.[26], mp 113.5 to 114.5°). A solid (1.08 g, 27%) was obtained on eluting the column with 1:1 mixture of petroleum ether-benzene, and this solid material was identified as cyclotridecanol, mp 58-60°, phenyl urethane, mp and mixed mp 84° (lit.[27] alcohol mp, 60-60.5°; phenyl urethane, mp 84-85°). Elution of the column with 1:3 mixture of petroleum ether-benzene gave 0.62 g (15%) of trans-1,2-cyclo-tridecane diol, mp 79-80° (lit.[28], mp 80-81°). Finally, 0.60 g (14%) of cis-1,2-cyclotridecane diol, mp 129-130° (lit.[28],

mp 130-131°) was obtained on eluting the column with ether.
Authenticity of the isomeric diols was established by comparison
of IR spectra and mixed mp with authentic samples.

Anal. for $C_{13}H_{26}O_2$: Calcd: C, 72.89; H, 12.15.

for cis-diol: Found: C, 72.85; H, 12.23.

for trans-diol: Found: C, 72.94; H, 12.00.

Column was ultimately drained with methanol to obtain 0.15 g (3%)
of a viscous oil which could not be crystallized at all. IR
spectrum showed the presence of only alcoholic group. TLC showed
two spots whose R_f values corresponded well with the diols
obtained from the hydroboration of 3-hydroxyclotridecene. On
the basis of these facts, this product has been tentatively
assigned as a mixture of isomeric 1,3-cyclotridecane diols.

Dihydroboration-Hydrolysis-Oxidation (Alkaline Hydrogen Peroxide) of 1,2-Cyclotridecadiene

1,2-Cyclotridecadiene (0.89 g, 0.005 mol)was hydroborated
with 3 ml of 2.4M of borane solution. The mixture of organobo-
ranes was allowed to stir with 20 ml of sodium hydroxide (0.8 g,
0.02 mol) solution at 80° for 24 hr. The reaction mixture was
then cooled to 0° and oxidized using 20 ml of 30% hydrogen
peroxide. The usual work-up procedure gave 70 mg (7%) of a
17:83 mixture of cis- and trans-cyclotridecene and 0.56 g (60%)
of cyclotridecanol.

Dihydroboration-Oxidation (Chromic trioxide in Pyridine) of 1,2-Cyclotridecadiene

A solution of pyridine complex of chromium trioxide (CrO_3)

was obtained by adding chromium trioxide (1.00 g, 0.01 mol) to a magnetically stirred solution of pyridine (1.58 g, 0.02 mol) in 25 ml of methylene dichloride and the reaction mixture was allowed to stir for 15 min. The solution was added to the organoboranes prepared from 1,2-cyclotridecadiene (0.89 g, 0.005 mol) in 10 ml of dry tetrahydrofuran and 3 ml of 2.4 ml borane solution and stirred for 2 hr. The usual isolation procedure gave 0.45 g (50%) of a mixture of cis-cyclotridecene and trans-cyclotridecene in the ratio 15:85 and 60 mg (3%) of cyclotridecanone.

Dihydroboration-Oxidation of 1,2-Cyclononadiene

Following the general procedure described for the hydroboration of 1,2-cyclotridecadiene, 1,2-cyclononadiene (1.84 g, 0.015 mol) was hydroborated using 26 ml of 0.8M borane (0.02 mol of borane) solution. The usual work-up afforded 1.22 g of crude product which on column chromatographic separation provided 0.012 g (0.60%) of trans-cyclononene, 6 mg (0.3%) of cyclononane (semicarbazone[29] mp and mixture mp, 185°) 0.67 g (31%) of cyclo-nonanol (mp and mixture mp of p-nitrobenzoate,[27] 82°), 0.25 g (11%) of cis-1,2-cyclononane diol (mp and mixture mp of bis-p-nitrobenzoate,[30] 126-128°) 0.25 g (11%) of trans-1,2-cyclononane diol (mp and mixture mp of bis-p-nitrobenzoate,[30] 176°) and 20 mg (1.5%) of trans-1,3-cyclononane diol (mp and mixture mp of bis-p-nitrobenzoate, 184-186°).

Anal. for $C_{23}H_{24}N_2O_8$: Calcd: C, 60.50; H, 5.20; N, 6.14.
Found: C, 60.30; H, 5.50; N, 5.96.

Dihydroboration-Oxidation of 3-Ethyl-1,2-pentadiene

Following the general procedure for dihydroboration, 3-ethyl-1,2-pentadiene (1.5 g, 0.016 mol) was hydroborated with 9 ml of 2.4M borane solution in tetrahydrofuran. The crude product (1.0 g) obtained after usual oxidation and work-up was chromatographed on basic alumina to get 0.14 g (7%) of 3-ethyl-2-pentanol[31] and 0.01 g (40%) of 3-ethyl-1,2-pentane diol.

The IR spectrum of 3-ethyl-2-pentanol showed absorptions at 3500 and 1035 cm^{-1} due to hydroxyl group. Its NMR spectrum had bands at δ 3.9 (m, 1H) hydroxyl bearing methine, and 0.9-1.5 (m, 15H).

Anal. for $C_7H_{16}O$: Calcd: C, 72.41; H, 13.80.

Found: C, 72.13; H, 13.57.

3-Ethyl-1,2-pentane diol exhibited IR bands due to hydroxyl, and displayed NMR bands at δ 3.5-3.9 (m, 3H) hydroxyl bearing methine and methylene, 3.6 (bs, 2H) hydroxyl and 1.0-1.4 (m, 11H) rest of the protons.

Anal. for $C_7H_{16}O_2$: Calcd: C, 63.63; H, 12.12.

Found: C, 63.32; H, 12.01.

Dihydroboration-Oxidation of 3-Phenyl-1,2-butadiene

The organoboranes prepared from dihydroboration of 3-phenyl-1,2-butadiene (1.95 g, 0.015 mol) and 12 ml of 2.4M borane solution in tetrahydrofuran on oxidation with alkaline hydrogen peroxide gave 1.5 g of crude product. The column chromatographic separation of the crude product on basic alumina

afforded 0.24 g (11%) of 3-phenyl-2-butanol, 0.16 g (7%) of 3-phenyl-1-butanol,[32] 0.2 g (8%) of 3-phenyl-1,3-butane diol[33] and 0.9 g (60%) of 3-phenyl-1,2-butane diol.

The purity of each product was checked by TLC, and their IR spectra indicated characteristic absorption bands for hydroxyl group.

The NMR spectrum of 3-phenyl-2-butanol displayed bands at δ 7.3 (s,5H) aromatic, 3.8 (q, J = 6 Hz, 1H) hydroxyl bearing methine proton, 2.82 (q, J = 7 Hz, 1H) benzilic proton 1.75 (s,1H) hydroxyl, 1.3 (d, J = 7 Hz, 3H) methyl and 1.0 (d, J = 6 Hz, 3H) methyl protons.

The compound on oxidation gave 3-phenyl-2-butanone which was identical in all respects with an authentic sample.[34]

Anal. for $C_{10}H_{14}O$: Calcd: C, 80.00; H, 9.33.

Found: C, 80.20; H, 9.09.

The NMR spectrum 3-phenyl-1-butanol showed signals at δ 7.5 (s, 5H) aromatic, 3.5 (t, J = 6 Hz, 2H) hydroxyl bearing methylene, 2.92 (q, J = 7 Hz, 1H) benzylic, 1.84 (t, J = 6 Hz, 2H) methylene, 1.75 (bs, 1H) hydroxyl, and 1.35 (d, J = 7 Hz, 3H) methyl protons.

Anal. for $C_{10}H_{14}O$: Calcd: C, 80.00; H, 9.33.

Found: C, 80.12; H, 9.18.

The NMR spectrum of 3-phenyl-1,3-butane diol exhibited signals at δ 7.45 (s, 5H) aromatic, 4.35 (bs, 1H) hydroxyl,

3.50 (m, 2H) methylene, 3.2 (bs, 1H) hydroxyl and 1.5 (s, 3H)
methyl protons.

Anal. for $C_{10}H_{14}O_2$: Calcd: C, 72.29; H, 8.43.

Found: C, 71.90; H, 8.40.

The NMR spectrum of 3-phenyl-1,2-butane diol had signals
at δ 7.3 (s, 5H) aromatic, 3.5-4.0 (bs, 2H) hydroxyl, 3.65 (m, 1H)
benzylic, 3.3 (m, 2H) hydroxyl bearing methylene, 2.63 (m, 1H)
hydroxyl bearing methine and 1.3 (d, J = 7 Hz, 3H) methyl protons.

Anal. for $C_{10}H_{14}O_2$: Calcd: C, 72.29; H, 8.43.

Found: C, 71.98; H, 8.35.

Dihydroboration-Oxidation of Phenylpropadiene

The procedure described for dihydroboration-oxidation of
1,2-cyclotridecadiene was followed. From phenylpropadiene
(1.16 g, 0.01 mol) and 0.01 mol of 2M borane, there was obtained
35 mg (2.5%) of 1-phenyl-1-propanol,[35] 0.1 g (7.5%) of 1-phenyl-
2-propanol,[36] 80 mg (5%) of 3-phenyl-1-propanol[37] and 0.42 g (38%)
of 1-phenyl-1,3-propane diol[33] after oxidation and work-up
procedure. The products were identified by comparison of GLC
retention times and IR spectra with those of authentic samples.

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CHAPTER IV

SYNTHESIS AND PROTONOLYSIS
OF SOME ALLYL ORGANOBORANES[1]

IV.1 ABSTRACT

Allyl organoboranes have been synthesized in situ by monohydroboration of monosubstituted and 1,1-disubstituted allenes (1,2-octadiene, 3-ethyl-1,2-pentadiene, phenylpropadiene and 3-phenyl-1,2-butadiene) with disiamylborane. It has been shown that these allyl organoboranes undergo allylic rearrangement during protonolysis to form terminal olefins. The formation of the terminal olefin is visualized through a six-membered cyclic transition state involving hydroxyl oxygen of the carboxylic acid. The procedure finds use in the synthesis of terminal olefins.

IV.2 INTRODUCTION

The organoboranes are relatively stable to aqueous acids and bases, but they undergo protonolysis by carboxylic acids with surprising ease. Consequently, the combined hydroboration-protonolysis offers a convenient noncatalytic route for the hydrogenation of carbon-carbon double bonds[2,3] (Scheme 1).

Scheme 1

$$R-CH=CH_2 \longrightarrow R-CH_2-CH_2-B\Big\langle \xrightarrow{CH_3COOH} R-CH_2-CH_3$$
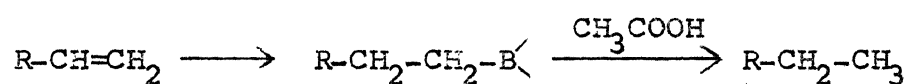
A detailed study of the action of carboxylic acids on trialkyl organoboranes has revealed that two of the three groups can be removed by excess of anhydrous acid at room temperature, and all three groups can generally be removed by refluxing the organoborane in diglyme solution with a moderate excess of propionic acid for 2 to 3 hours.

Among the structural variations in the trialkylboranes with respect to the action of carboxylic acids it has been demonstrated that a secondary alkyl group undergoes protonolysis less readily than primary. Consequently, in hydrogenating internal olefins containing bulky groups it is preferable that the boron atom be transferred to the terminal position by heating under reflux prior to the addition of acid. The procedure has also been applied for the hydrogenation of olefins containing

active sulfur, chlorine and nitrogen substituents. Allylmethyl-sulfide has readily been converted by hydroboration-protonolysis to n-propylmethylsulfide in good yield.[3] The reaction proceeds with retention in configuration. Thus, tri-exo-norbornylborane undergoes deuterolysis to yield exo-deuteronorbornane[4] (Scheme 2).

<u>Scheme 2</u>
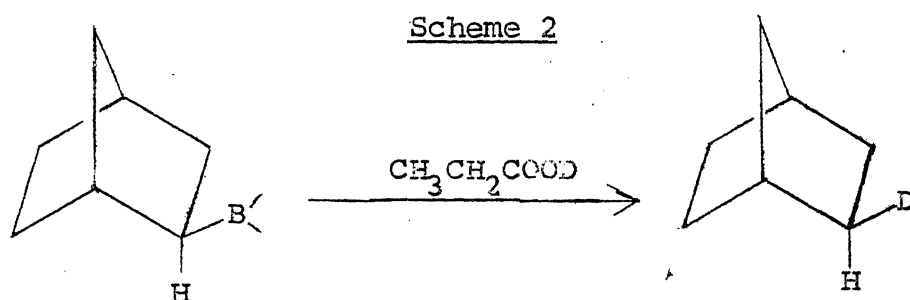
Further, the hydroboration-protonolysis reaction occurs in a cis manner involving the less hindered side of the double bond.[4]

Vinyl organoboranes, readily available through monohydro-boration of acetylenes undergo protonolysis much more readily at room temperature and the reaction provides a convenient means of converting acetylene into cis olefin of high purity[5-7] (Scheme 3).

<u>Scheme 3</u>
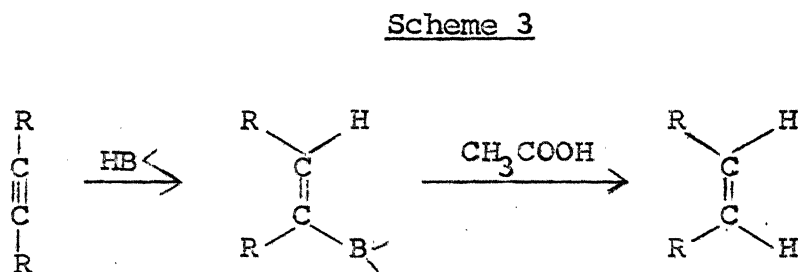
It has been shown that monohydroboration of cyclic allenes with disiamylborane (Sia_2BH) results in the attack of boron primarily at the central carbon atom of the allenic linkage to yield vinylborane predominantly.[8,9] The protonolysis of the intermediate organoboranes has been achieved to provide cyclic olefins (Scheme 4).

Scheme 4

$(CH_2)_n$ $\begin{matrix} CH \\ \| \\ C \\ \| \\ CH \end{matrix}$ $\xrightarrow{\begin{matrix} 1.Sia_2BH \\ \hline 2.CH_3COOH \end{matrix}}$

n = 7, 10

$(CH_2)_8$ $\begin{matrix} CH \\ \| \\ CH \end{matrix}$

cis 100%

$(CH_2)_{11}$ $\begin{matrix} CH \\ \| \\ CH \end{matrix}$ + $(CH_2)_{11}$ $\begin{matrix} HC \\ \| \\ CH \end{matrix}$

cis 74%   trans 26%
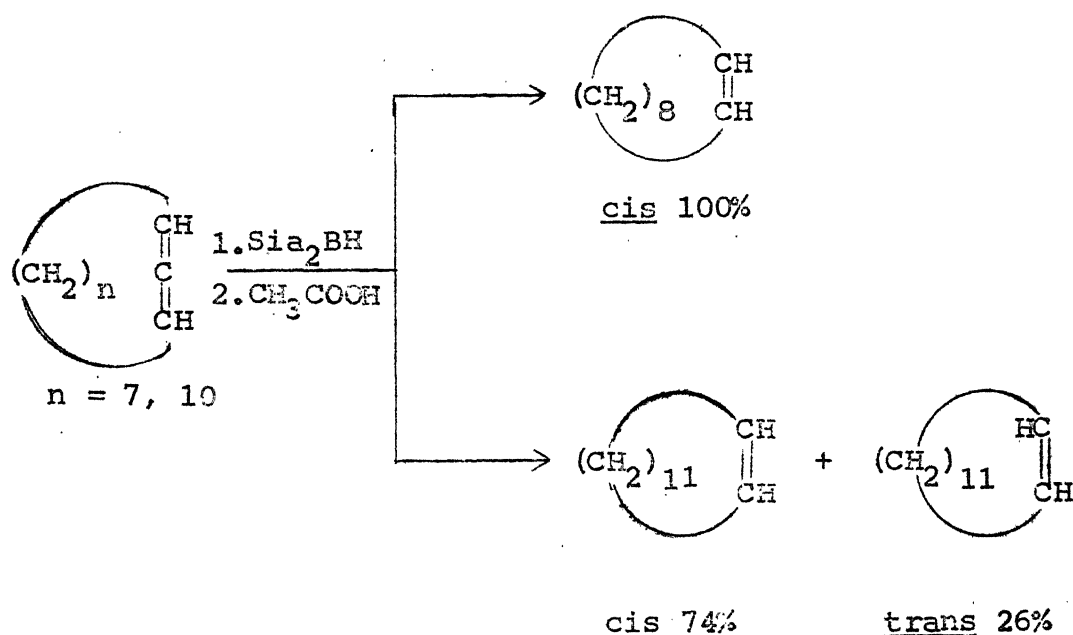
The unique effectiveness of carboxylic acids must be due to the structure of carboxylic acid group. The trialkyl organoborane is capable of coordinating at the oxygen of the carbonyl group, placing boron-carbon bond in position for an intramolecular attack by the proton. The increasing difficulty at each

corresponding olefins[13] (Scheme 7).

Scheme 7

n = 1,2,4

n = 6,7
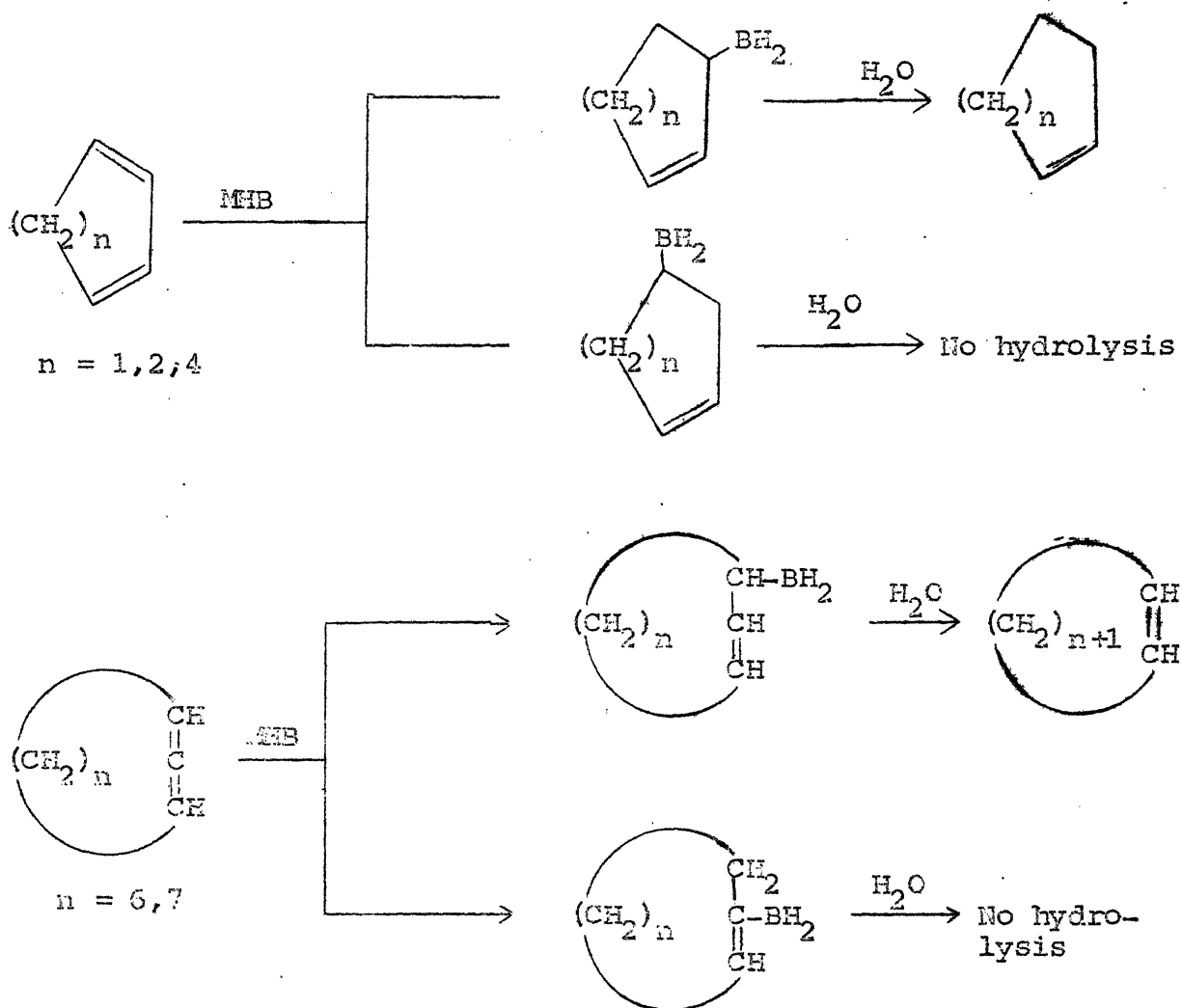
The results with monohydroboration-oxidation of representative mono- and 1,1-disubstituted acyclic allenes suggest that the attack of boron is primarily at the methylene carbon atom of the allenic linkage to yield allyl organoboranes when disiamylborane is used as the hydroborating agent.[14] The

observed selectivity could solely be dictated by the steric requirement of the allene in the well known transition state for hydroboration postulated by Brown[15] (Scheme 8). So it became

Scheme 8
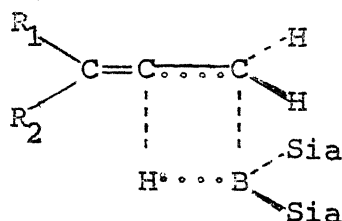
desirable to explore the behaviour of allylic organoboranes towards carboxylic acids. In view of this, 1,2-octadiene, 3-ethyl-1,2-pentadiene, phenylpropadiene, and 3-phenyl-1,2-butadiene were synthesized and subjected to hydroboration with disiamylborane followed by protonolysis. The advantage of using disiamylborane is two-fold. Firstly, it leads to the formation of 3-substituted and 3,3-disubstituted allylic organoboranes as major products. Secondly, it would enable one to compare the reactivity of the alkyl group with that of an allyl group attached to the same boron, and thereby observe allylic rearrangement, if any, during the reaction with acetic acid.

IV.3 RESULTS AND DISCUSSION

All allenes were synthesized by the best route available to-date which involves two-step sequence starting from an olefin. In this two-step sequence, the first step is the addition of

dibromocarbene to an olefin and second step is the reaction of the resulting 1,1-dibromocyclopropane derivative with methyl-lithium in ether at -40 to -45° to obtain allene in good yield.[16,17] The acyclic allenes, 1,2-octadiene ($\underline{1}$), 3-ethyl-1,2-pentadiene($\underline{2}$), phenylpropadiene ($\underline{3}$) and 3-phenyl-1,2-butadiene ($\underline{4}$) used in the present investigation were prepared by the above method(Scheme 9).

Scheme 9

$$R_1 = \underline{n}\text{-}C_5H_{11}; \quad R_2 = R_3 = R_4 = H \qquad \underline{1}$$

$$R_1 = R_2 = C_2H_5; \quad R_3 = R_4 = H \qquad \underline{2}$$

$$R_1 = C_6H_5; \quad R_2 = R_3 = R_4 = H \qquad \underline{3}$$

$$R_1 = C_6H_5; \quad R_2 = CH_3; \quad R_3 = R_4 = H \qquad \underline{4}$$
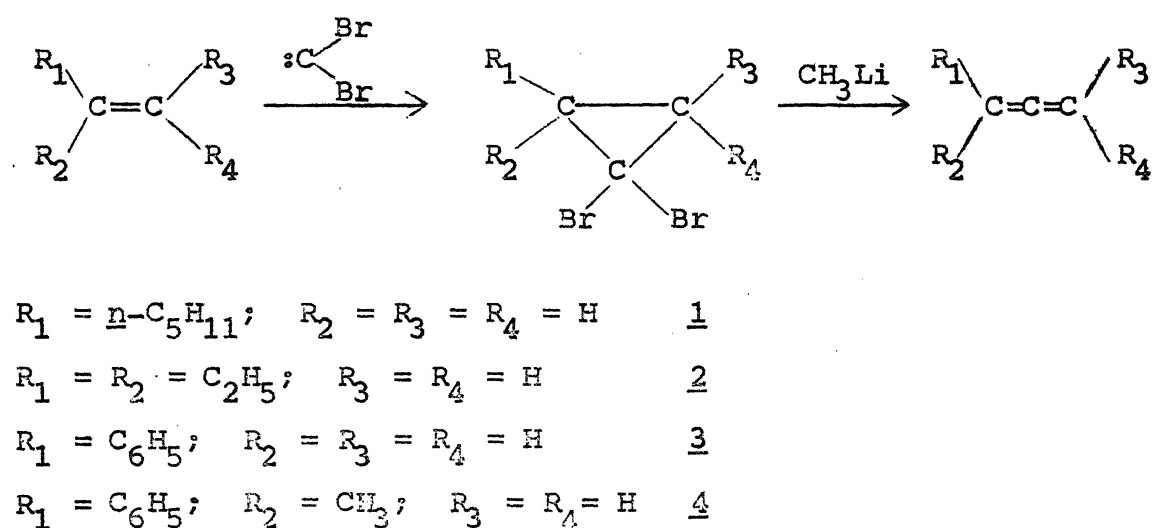
The identity of cyclopropane derivatives prepared from the corresponding olefins was thoroughly established by analytical and physical data. Allenes synthesized from the dibromo-compounds showed characteristic absorptions in IR at 1950 and 850 cm^{-1} due to antisymmetrical $>$C=C=C$<$ stretching vibration and torsional motion of an allenic terminal methylene respectively.[18] The purity of the allenes was checked by GLC on a carbowax column and the properties observed agreed with those reported in the literature.

Disiamylborane (Sia_2BH) was prepared by the hydrobora-
tion of 2-methyl-2-butene under a static pressure of dry
nitrogen.[19] A solution of appropriate allene in diglyme was
added to the above solution within 5 min. The mixture was
allowed to attain room temperature (approx. 3 hr). The resulting
organoboranes were treated with glacial acetic acid at room tempe-
rature or $80°$ for 24 hr and worked-up in the usual manner to
obtain olefinic product(s) in each case.[5]

The hydroboration-protonolysis of 1,2-octadiene (1) at
room temperature afforded an olefinic mixture in 38% yield.
The composition of the olefinic mixture as established by GLC
on a 15 ft propylene glycol-silver nitrate column was 82%
1-octene (5), 8% cis-2-octene (6) and 10% trans-2-octene (7)
(Scheme 10). The protonolysis of the intermediate organoboranes

Scheme 10

$$n-C_5H_{11}-CH=C=CH_2 \quad \xrightarrow[\substack{\text{AcOH} \\ \text{r.t.} \\ 24 \text{ hr}}]{Sia_2BH}$$

1

$$n-C_6H_{13}-CH=CH_2 \quad (82\%)$$
5

$$\underset{H}{\overset{n-C_5H_{11}}{>}}C=C\underset{H}{\overset{CH_3}{<}} \quad (8\%)$$
6

$$\underset{H}{\overset{n-C_5H_{11}}{>}}C=C\underset{CH_3}{\overset{H}{<}} \quad (10\%)$$
7
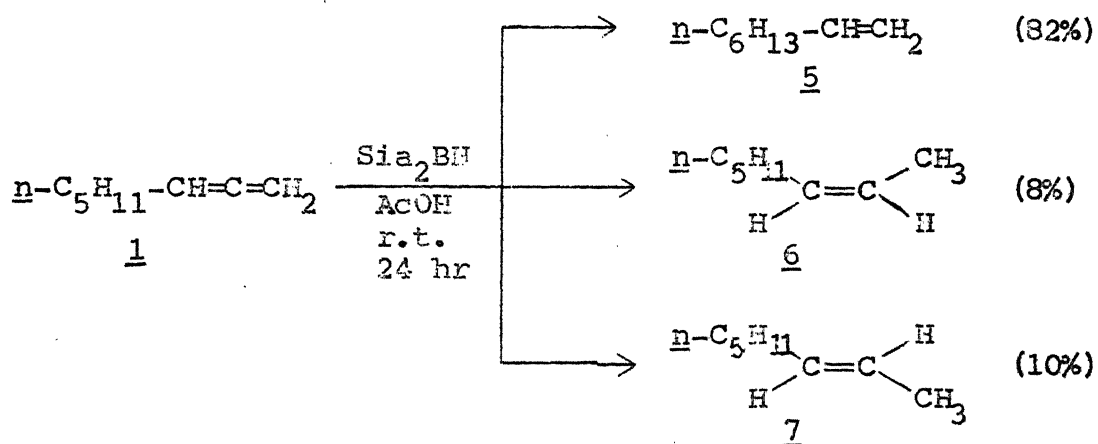
from 1,2-octadiene (1) at $80°$ for 24 hr gave the same olefinic
mixture in somewhat better yield (65%). The protonolysis of

the organoboranes from 3-ethyl-1,2-pentadiene (2) gave an
olefinic mixture (20%) of 2% 3-ethyl-2-pentene (8) and 98%
3-ethyl-1-pentene (9) (Scheme 11). Phenylpropadiene (3) was
hydroborated with disiamylborane and protonated with acetic
acid at room temperature to give an olefinic mixture of allylben-
zene (10) and cis-propenylbenzene (11) in the ratio 91:9
(Scheme 12). The GLC analysis of the mixture was done on a

Scheme 11

$$C_2H_5 \diagdown C=C=CH_2 \quad \xrightarrow[\substack{\text{AcOH} \\ \text{r.t.} \\ \text{24 hr}}]{Sia_2BH} \quad$$

$$C_2H_5 \diagup \underline{2}$$

$(C_2H_5)_2C=CH-CH_3 \qquad (2\%)$
$$\underline{8}$$

$(C_2H_5)_2CH-CH=CH_2 \qquad (98\%)$
$$\underline{9}$$

Scheme 12

$$C_6H_5-CH=C=CH_2 \quad \xrightarrow[\substack{\text{AcOH} \\ \text{r.t.} \\ \text{24 hr}}]{Sia_2BH} \quad$$

$$\underline{3}$$

$C_6H_5-CH=CH_2 \qquad (91\%)$
$$\underline{10}$$

$$C_6H_5 \diagdown C=C \diagup CH_3$$
$$H \diagup \underset{\underline{11}}{} \diagdown H \qquad (9\%)$$
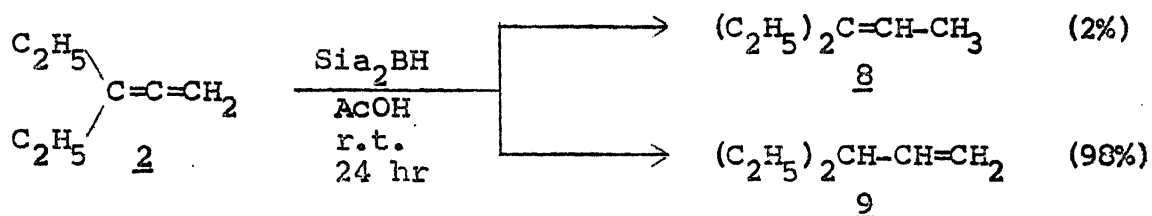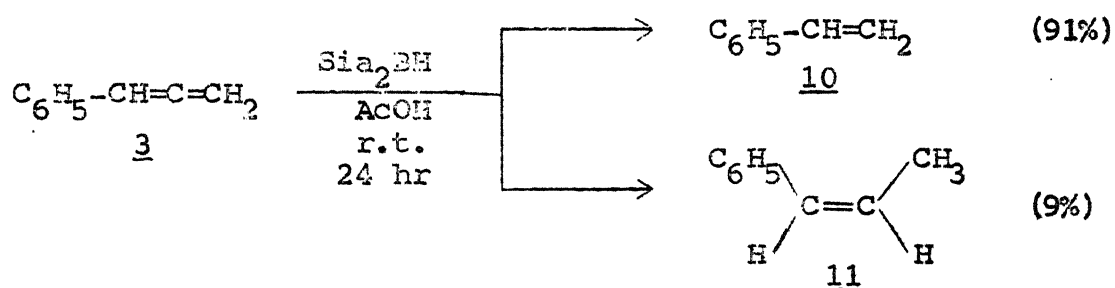
10 ft carbowax column. Protonolysis at 80° for 2 hr provided
in 28% yield an olefinic mixture, which showed the presence of
8% n-propylbenzene (12), 8% allylbenzene (10), 74% cis-propenyl-
benzene (11) and 10% trans-propenylbenzene (13) (Scheme 13).

Scheme 13

$C_6H_5-CH=C=CH_2$ $\xrightarrow[\substack{AcOH \\ 80^\circ \\ 2\ hr}]{Sia_2BH}$

3

$\longrightarrow\ C_6H_5-CH_2-CH_2-CH_3$ (8%)
12

$\longrightarrow\ C_6H_5-CH_2-CH=CH_2$ (8%)
10

$\longrightarrow$
$$\underset{H}{\overset{C_6H_5}{\diagdown}}C=C\underset{H}{\overset{CH_3}{\diagup}}$$
(74%)

11

$\longrightarrow$
$$\underset{H}{\overset{C_6H_5}{\diagdown}}C=C\underset{CH_3}{\overset{H}{\diagup}}$$
(10%)

13

The product (27%) obtained from the hydroboration-proto-
nolysis of 3-phenyl-1,2-butadiene (**4**) was found to be single.
Spectral analyses (IR and NMR) of the product showed it to be
3-phenyl-1-butene (**14**) (Scheme 14). The hydroboration of
3-phenyl-1,2-butadiene (**4**) followed by the treatment with
deuterated acetic acid yielded 3-phenyl-3-D-1-butene (15)
(Scheme 14). There was not much improvement in the yield when
it was carried out at 80°.

Scheme 14

$$\underset{H_3C}{\overset{C_6H_5}{\diagdown}}C=C=CH_2$$
4

$\xrightarrow{Sia_2BH}$

$\xrightarrow{AcOH}$
$$\underset{H_3C}{\overset{C_6H_5}{\diagdown}}CH-CH=CH_2$$
14

$\xrightarrow{AcOD}$
$$\underset{H_3C}{\overset{C_6H_5}{\diagdown}}CD-CH=CH_2$$
15

Scheme 13

$$C_6H_5\text{-}CH=C=CH_2 \quad \xrightarrow[\substack{AcOH \\ 80^\circ \\ 2\ hr}]{Sia_2BH}$$

3

$C_6H_5\text{-}CH_2\text{-}CH_2\text{-}CH_3$ (8%)

12

$C_6H_5\text{-}CH_2\text{-}CH=CH_2$ (8%)

10

$$\underset{H}{\overset{C_6H_5}{>}}C=C\underset{H}{\overset{CH_3}{<}}$$ (74%)

11

$$\underset{H}{\overset{C_6H_5}{>}}C=C\underset{CH_3}{\overset{H}{<}}$$ (10%)

13

The product (27%) obtained from the hydroboration-proto-nolysis of 3-phenyl-1,2-butadiene (4) was found to be single. Spectral analyses (IR and NMR) of the product showed it to be 3-phenyl-1-butene (14) (Scheme 14). The hydroboration of 3-phenyl-1,2-butadiene (4) followed by the treatment with deuterated acetic acid yielded 3-phenyl-3-D-1-butene (15) (Scheme 14). There was not much improvement in the yield when it was carried out at 80°.

Scheme 14

$$\underset{H_3C}{\overset{C_6H_5}{>}}C=C=CH_2 \quad \xrightarrow{Sia_2BH}$$

4

AcOH

$$\underset{H_3C}{\overset{C_6H_5}{>}}CH\text{-}CH=CH_2$$

14

AcOD

$$\underset{H_3C}{\overset{C_6H_5}{>}}CD\text{-}CH=CH_2$$

15

Figure IV.1 NMR spectrum of 3-phenyl-3-D-1-butene (15)
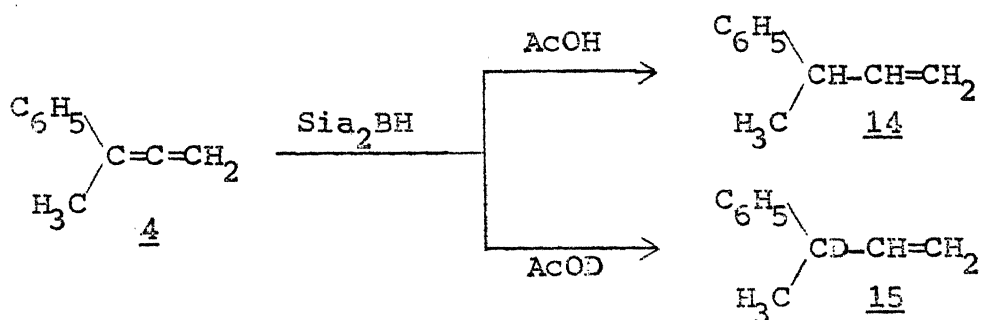
The identity of all the products was established by comparison of GLC retention times and IR spectra with those of authentic sample. Wherever necessary, NMR spectra were also used in the characterization of the products.

The results are summarized in Table 1. A general scheme for the monohydroboration-protonolysis of acyclic allenes studies is represented in Scheme 15.

Scheme 15

$$\underset{/}{\overset{\backslash}{C}}=C=CH_2 \quad \xrightarrow{Sia_2BH} \quad \underset{/}{\overset{\backslash}{C}}=CH-CH_2-BSia_2 \quad \xrightarrow{CH_3COOH} \quad \underset{/}{\overset{\backslash}{C}}H-CH=CH_2$$
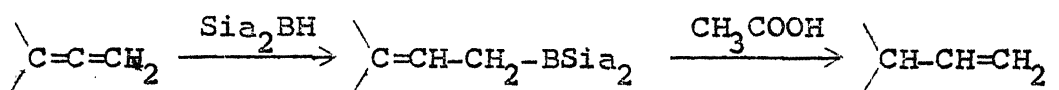
Table 1

Allene	Product Composition	Yield* (%)
1,2-Octadiene	1-Octene (82%)	
	cis-2-Octene (8%)	38
	trans-2-Octene (10%)	
3-Ethyl-1,2-penta-diene	3-Ethyl-1-pentene (98%)	20
	3-Ethyl-2-pentene (2%)	
Phenylpropadiene	Allylbenzene (91%)	25
	cis-propenylbenzene (9%)	
3-Phenyl-1,2-buta-diene	3-Phenyl-1-butene (100%)	27

* Protonolysis carried our at r.t.

The results given in Table 1 suggest that the protono-
lysis of the initially formed allyl organoboranes proceeds with
rearrangement.[20-22] The fact that 3-phenyl-3-D-1-butene (15)
is formed during the reaction of the organoborane from 3-phenyl-
1,2-butadiene (4) with deuterated acetic acid confirms the
allylic rearrangement during protonolysis. The other possible
route for the formation of the terminal olefin is by the protono-
lysis of the vinylic organoborane obtained by the electrophilic
attack of the boron at the central carbon atom of the allene via
the four centered transition state as shown in Scheme 16. The
fact that no 3-phenyl-1-D-1-butene could be traced by NMR from
monohydroboration-protonolysis of 3-phenyl-1,2-butadiene (4),
excludes this possibility in the case of 1,1-disubstituted
allenes (2 and 4). However, our results do not exclude this
path for the formation of a small amount of terminal olefin in
the case of 1,2-octadiene (1) or phenylpropadiene (3).

<u>Scheme 16</u>

$$R = -CH-CH(CH_3)_2$$
$$\quad\; |$$
$$\quad CH_3$$
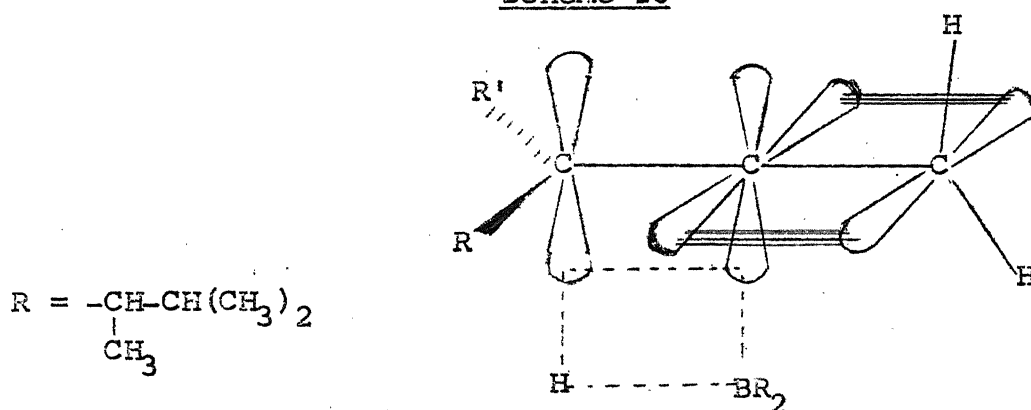
The formation of internal olefins as minor products in
the case of monosubstituted allenes (1 and 3) in particular may

arise from either protonolysis of the vinylic organoborane
obtained by addition of ⟩B-H to the terminal double bond of
the allene via the four centered transition state (Scheme 17)
and/or protonolysis of allyl organoborane without rearrangement.

Scheme 17

R = -CH-CH(CH₃)₂
     |
     CH₃
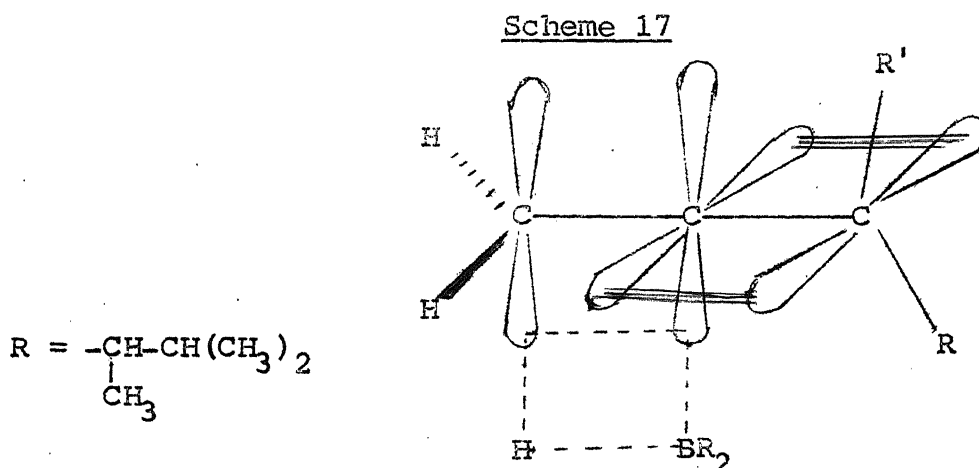
The yield of the product increases on carrying out the
reaction at 80°. However, an attempt to increase the yield in
the case of phenylpropadiene (3) by carrying out the protono-
lysis at 80° for 2 hr resulted in the formation of 8% n-propyl-
benzene (12), 8% allylbenzene (10), 74% cis-propenylbenzene (11)
and 10% trans-propenylbenzene (13) (Scheme 13). These results
suggest that the isomerization of the initially formed allyl
organoborane to vinyl organoborane has occurred prior to proto-
nolysis. In the light of this we feel that the ready isomeri-
sation of the allyl organoborane from phenylpropadiene (3) may
be attributed to the favourable four-membered transition state
for the formation of vinyl organoborane after elimination
process based on electronic as well as steric factors. The

formation of cis-propenylbenzene (11) as the major product
after protonolysis indicates that the disiamylborane approaches
phenylpropadiene (4) from the least hindered hydrogen side as
shown in the Scheme 18.

Scheme 18

R = CH-CH(CH₃)₂
     |
     CH₃
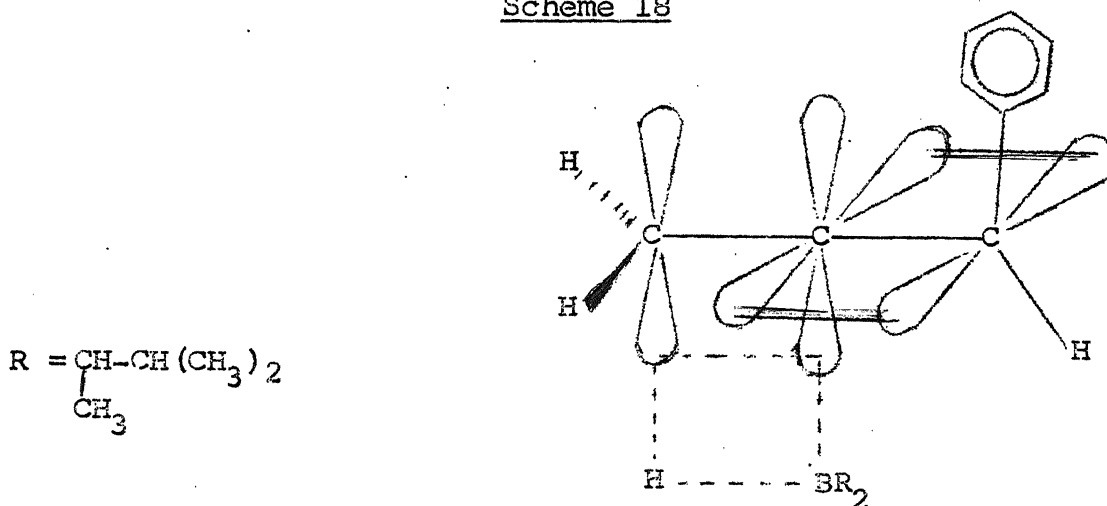
The formation of terminal olefins during the protonolysis
of the various allyl organoboranes can be visualized through a
six-membered cyclic transition state involving hydroxyl oxygen
of the carboxylic acid.[23] However, the eight-membered cyclic
transition state which involves carbonyl oxygen or the non-
cyclic S_E2' process similar to one proposed for allylic
Grignard reagent cannot be ruled out at present, but is less
likely[24] (Scheme 19). The yields of the products are not
improved by the addition of a base like sodium acetate in a
buffer. This observation suggests that S_E2' process is less
likely. The low yields of the olefins may be due to competi-
tive protonolysis of the alkyl group versus allyl group.[2] Our
results do not permit us to comment on the comparative reactivity

of the substituted allyl group and siamyl group during

Scheme 19

R = -CH-CH(CH$_3$)$_2$
       |
       CH$_3$
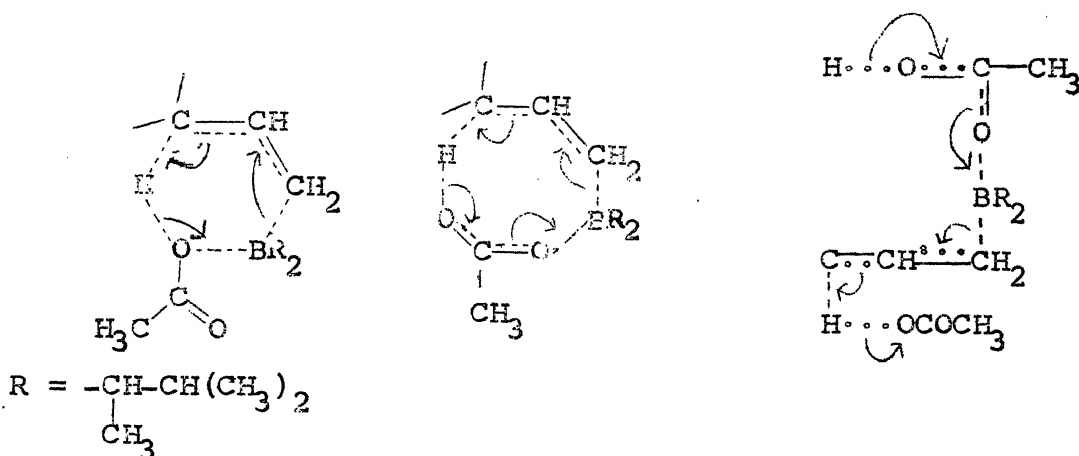
protonolysis as the amount of isopentane formed has not been detected. The slow reactivity of allyl organoboranes as compared to vinyl organoboranes toward protonolysis may be due to the less basic oxygen function involved in a six-membered transition state in the case of allyl organoborane (Scheme 20).

Scheme 20

Very recently similar allylic rearrangement has been described by Brown and Nambu[21] in the reaction of triethylborane (18) with ethyl-4-bromocrotonate (17) in presence of potassium 2,6-di-t-butylphenoxide (16). The formation of the isomeric ethyl 3-hexenoate (20) instead of the anticipated ethyl 2-hexenoate results from an allylic migration of the double bond. The unusual migration of the double bond observed in this reaction presumably takes place during the protonolysis of the intermediate organoborane (19) as indicated in Scheme 21.

Scheme 21

$$\overset{-}{\underset{16}{O}}\overset{+}{K} + CH_2BrCH=CHCO_2C_2H_5 \longrightarrow K\overset{+}{C}\overline{HBrCH}=CHCO_2C_2H_5 + OH$$

$$\underset{17}{}$$

$$Et_3B + \left[CHBrCH=CHCO_2C_2H_5\right]^-\overset{+}{K} \longrightarrow \left[Et_3B-\overset{\overset{Br}{|}}{CH}-CH=CHCO_2C_2H_5\right]^-\overset{+}{K}$$

$$\underset{18}{}$$

$$\left[Et_2B-\overset{Et}{CH}-CH=CHCO_2C_2H_5\right]^+_{Br}\overset{-}{K} \longrightarrow Et_2B-\overset{\overset{Et}{|}}{CH}-CH=CHCO_2C_2H_5 + KBr$$

$$\underset{19}{}$$

$$\overset{Et}{\diagdown}\underset{Et_2B}{\overset{}{CH}}-C\overset{\diagup H}{\diagdown}CHCO_2C_2H_5 \longrightarrow \overset{Et}{\diagdown}\underset{H}{C}=C\overset{\diagup H}{\diagdown}CH_2CO_2C_2H_5$$

$$\underset{}{R}\diagup\overset{}{O}\text{---}H \qquad\qquad \underset{20}{}$$
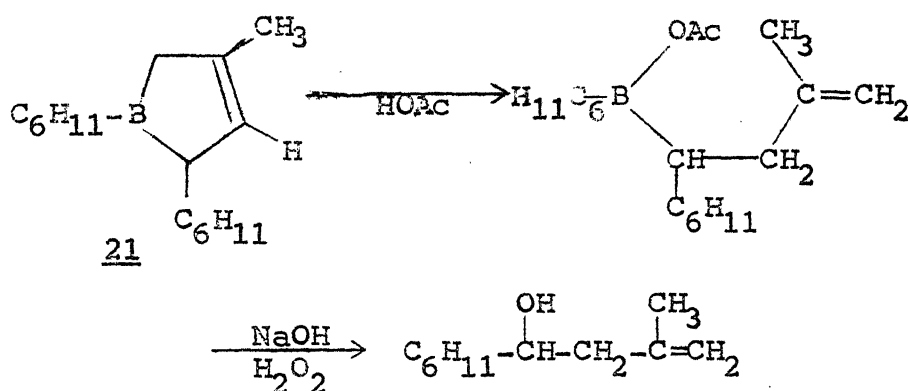
ROH = 2,6-di-t-butylphenol

Further Zweifel and others[22] have also noted the migration of the double bond during the protonolysis-oxidation of the bora-cyclopentene (21) (Scheme 22). It should be noted that the

Scheme 22

double bond migrates exclusively in one direction.

IV.4 EXPERIMENTAL

Boiling points are uncorrected. All infrared (IR) spectra were recorded on a Perkin-Elmer Model 700 spectrophotometer as thin films between sodium chloride plates. Nuclear magnetic resonance (NMR) spectra were taken on a Varian A-60 spectrometer in deuterated chloroform with TMS as the internal standard. Gas liquid chromatographic (GLC) analyses were done with Aerograph Model 90-P instrument using 5 or 10 or 15 ft by 1/4 inch column. The following liquid phases were employed (percentage by weight on 60/80 mesh chromosorb W): 15% carbowax 20 M,

15% carbowax, 20M-silver nitrate, 15% propylene glycol-silver nitrate and 15% ucon.

Starting Materials

Diglyme (Ansul Co.) was kept over calcium hydride for 24 hr, decanted and distilled from slight excess of lithium aluminium hydride under reduced pressure. Boron trifluoride ethyl etherate (Eastman) was treated with a small quantity of dry diethyl ether (to ensure an excess of this component) and distilled under reduced pressure over calcium hydride. Sodium borohydride from Metal Hydrides Inc. was used. 2-Methyl-2-butene (Aldrich Co.) was used for the preparation of disiamylborane. 1-Heptene (Aldrich Co.), 2-ethyl-1-butene (Aldrich Co.), styrene (BDH),α-methyl styrene (BDH) and glacial acetic acid (BDH) were used as such. Deuterated acetic acid was prepared from acetic anhydride and deuterated water.

The allenes other than 1,2-octadiene used in the present investigation were prepared by the procedure described earlier in Chapter III.4.

Preparation of 1,1-Dibromo-2-n-pentylcyclopropane

Following the general procedure described already in Chapter I.4,from 1-heptene (24.5 g, 0.25 mol), potassium (8 g, 0.20 g atom), 250 ml of dry t-butanol and bromoform (50.6 g, 0.20 mol), there was obtained 35 g (65%) of 1,1-dibromo-2-n-pentylcyclopropane, bp 64° at 0.07 mm.

The purity of the sample was confirmed by GLC. The IR spectrum showed the absence of olefinic bond. The compound was saturated to bromine and neutral potassium permanganate.

Preparation of 1,2-Octadiene

The treatment of methyllithium prepared from lithium (2.8 g, 0.40 g atom) and methyl iodide (28.0 g, 0.20 mol) with 1,1-dibromo-2-pentylcyclopropane (27.0 g, 0.10 mol) in dry ether provided 8.8 g (80%) of 1,2-octadiene, bp 65° at 60 mm, n_D^{30} 1.4336 (lit[24] bp 130° at 756 mm, n_D^{29} 1.4340).

The GLC analysis on a carbowax-silver nitrate column indicated it to be single substance. The compound possessed IR absorption bands at 1957 and 853 cm^{-1} characteristic of allenic group.

Monohydroboration-Protonolysis of 1,2-Octadiene

Pulverized sodium borohydride (1.06 g, 0.028 mol), 2-methyl-2-butene (4.9 g, 0.07 mol) and dry diglyme (28 ml) were placed in a 250 ml three-necked flask fitted with a condenser, an equilibrating dropping funnel, a thermometer and an inlet and an outlet for dry nitrogen gas. Hydroboration was carried out by adding boron trifluoride etherate (6.2 g, 0.04 mol, 10% excess) in diglyme (10 ml) at -5 to 0° over a period of 30 min. Throughout the reaction a static pressure of nitrogen gas was maintained. After allowing the reaction mixture to stand at 0° for 1 hr, 1,2-octadiene (3.85 g, 0.035 mol) was added within

5 min. The mixture was left for 3 hr to attain room temperature. Glacial acetic acid (10 ml) was added to the mixture and it was stirred at room temperature for 24 hr. The mixture was poured into ice-cold water, extracted with pentane, washed with water until neutral and dried over anhydrous magnesium sulphate. Distillation of the residue after removal of the solvent afforded 1.5 g (38%) of olefinic mixture with a bp 121-122° at 754 mm. GLC analysis on a 15 ft propylene glycol-silver nitrate column indicated the presence of 82% 1-octene, 8% cis-2-octene and 10% trans-2-octene. The identity of the products was established by comparison of GLC retention times and IR spectra with those of the authentic samples. The protonolysis of the organoborane at 80° for 24 hr improved the yield (65%). However, the distribution of the products was essentially the same.

Monohydroboration-Protonolysis of 3-Ethyl-1,2-pentadiene[25]

The procedure described for monohydroboration-protonolysis of 1,2-octadiene was followed without any change. From 3-ethyl-1,2-pentadiene (2.4 g, 0.025 mol), sodium borohydride (0.76 g, 0.02 mol), 2-methyl-2-butene (3.5 g, 0.05 mol) and boron trifluoride etherate (3.9 g, 0.027 mol), there was obtained 0.48 g (20%) of a mixture of olefins, bp 104-108° (bath temperature) at 754 mm. GLC analysis of the mixture on a 15 ft propylene glycol-silver nitrate column showed 98% 3-ethyl-1-pentene and 2% 3-ethyl-2-pentene. Only 3-ethyl-1-pentene[28] was separated by GLC and identified by comparison

of IR and NMR spectra with that of an authentic sample. The minor product was identified by comparison of GLC retention times with an authentic sample.

Monohydroboration-Protonolysis of Phenylpropadiene[26]

The organoboranes obtained from phenylpropadiene (2.3 g, 0.02 mol), sodium borohydride (0.57 g, 0.015 mol), 2-methyl-2-butene (2.8 g, 0.04 mol) and boron trifluoride etherate (3.10 g, 0.02 mol) on treatment with glacial acetic acid (10 ml) at room temperature for 24 hr afforded 0.6 g (25%) of a mixture of olefins, bp 75-80° (bath temperature) at 40 mm. The mixture contained 91% allylbenzene and 9% cis-propenylbenzene as analysed by GLC on a 10 ft carbowax column. The products were identified by comparison of their GLC retention times and IR spectra with those of authentic samples.

Protonolysis at 80° for 2 hr provided in 28% yield an olefinic mixture which showed the presence of n-propylbenzene (8%), allylbenzene (8%), cis-propenylbenzene (74%) and trans-propenylbenzene (10%).

Monohydroboration-Protonolysis of 3-Phenyl-1,2-butadiene[27]

Following the procedure described for 1,2-octadiene, from 3-phenyl-1,2-butadiene (2.6 g, 0.02 mol), sodium borohydride (0.57 g, 0.15 mol), 2-methyl-2-butene (2.8 g, 0.04 mol) and boron trifluoride etherate (3.12 g, 0.022 mol, 10% excess), was obtained 0.71 g (27%) of 3-phenyl-1-butene, bp 66-70° at 13 mm. GLC analysis indicated it to be a single component.

IR and NMR spectra were identical with those of an authentic
sample. IR spectrum had two bands at 990 and 920 cm^{-1} charac-
teristic of a monosubstituted olefin. NMR spectrum possessed
bands at δ 7.15 (s, 5H) aromatic protons, 5.98 (m, 1H) olefinic
proton, 5.0 (m, 2H) terminal olefinic protons, 3.40 (m, 1H)
benzylic and 1.30 (d, 3H, J = 6.5 Hz) methyl protons.

The organoborane obtained from 3-phenyl-1,2-butadiene,
when treated with deuterated acetic acid (from acetic anhydride
and deuterated water) afforded 3-phenyl-3-D-1-butene in 25% yield.
IR spectrum showed absorptions at 990 and 920 cm^{-1} characteris-
tic of a monosubstituted olefin. NMR spectrum had bands at
δ 7.15 (s, 5H) aromatic protons, 5.98 (dd, J_t= 17 and J_c= 9 Hz,
1H) olefinic proton, 5.0 (m, 2H) terminal olefinic protons and
1.30 (s, 3H) methyl protons.

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CHAPTER V
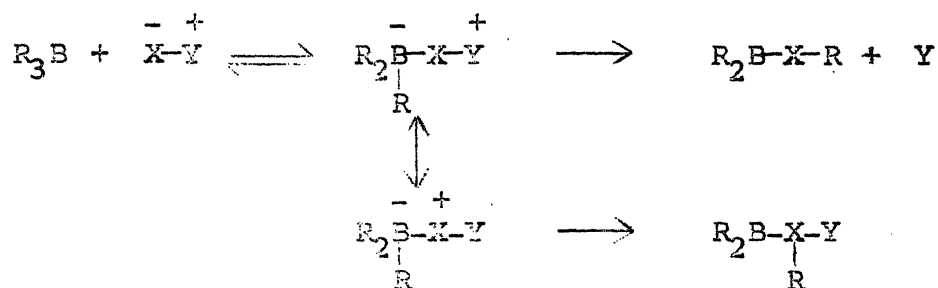
SYNTHESIS AND REACTION OF DISIAMYL-
(3-PHENYL-2-BUTENYL) BORANE [DSPBB]
WITH ALDEHYDES AND KETONES

V.I ABSTRACT

A substituted allyl organoborane, disiamyl(3-phenyl-2-butenyl)borane [DSPBB] has been synthesized in situ by monohydroboration of 3-phenyl-1,2-butadiene with disiamylborane. The DSPBB undergoes ready reaction with butyraldehyde, benzaldehyde, acrolein and acetone to give β,γ-unsaturated alcohols whose structures have been confirmed by elemental analysis, IR and NMR. Various experimental evidences suggest that the formation of the unsaturated alcohols can best be visualized through a six-membered cyclic transition state rather than a non-cyclic S_E2' process. Thus, the reaction of DSPBB with aldehydes and ketones could be used in a convenient synthesis of substituted β,γ-unsaturated sec- and tert-alcohols which in turn could be dehydrated to make substituted 1,4-dienes.

V.2   INTRODUCTION

Organoboranes are reactive intermediates involved in many new organic synthesis.   The majority of such reactions apparently arises from the fact that organoboranes exhibit a strong tendency to share an electron pair with a nucleophile. The coordination greatly increases the carbanion-like character of alkyl groups and thereby facilitates reactions in which an alkyl group is transferred with its electron-pair to the near-by positive atom (Scheme 1).
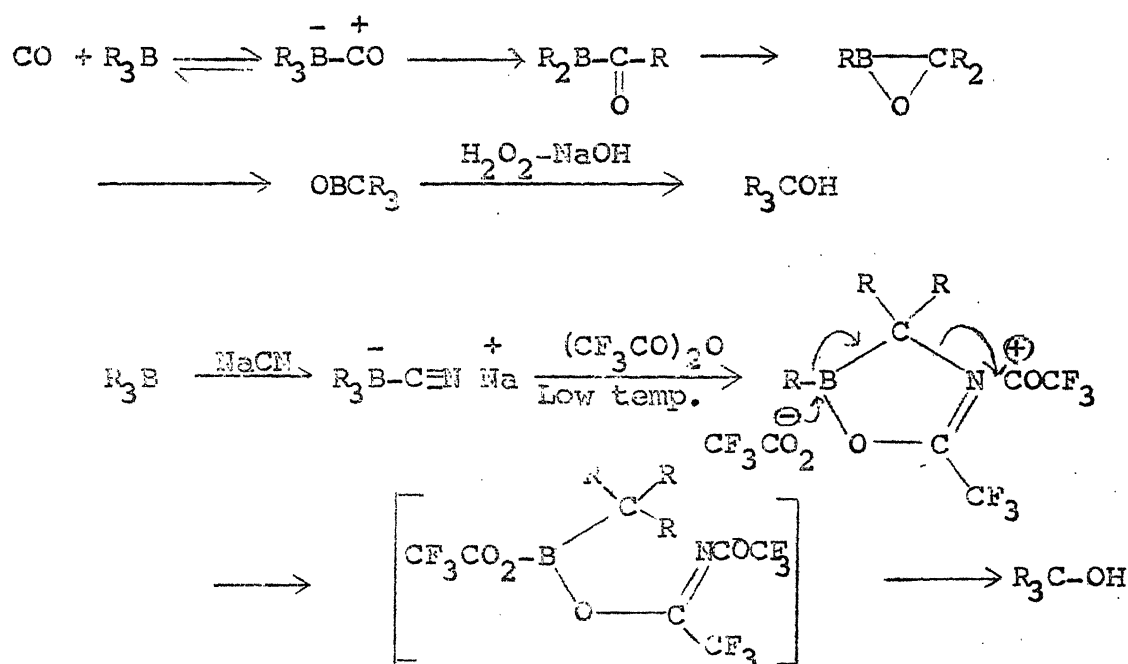
<center>Scheme 1</center>

$$R_3B \;+\; \overset{-}{X}\text{-}\overset{+}{Y} \;\rightleftharpoons\; \underset{\underset{R}{|}}{R_2\overset{-}{B}\text{-}\overset{+}{X}\text{-}Y} \;\longrightarrow\; R_2B\text{-}X\text{-}R \;+\; Y$$

$$\underset{\underset{R}{|}}{R_2\overset{-}{B}\text{-}\overset{+}{X}\text{-}Y} \;\longrightarrow\; \underset{\underset{R}{|}}{R_2B\text{-}X\text{-}Y}$$

With carbanion as nucleophile, it is possible to homologate the alkyl group(s) of the trialkyl organoborane.

The reaction of carbon monoxide with trialkylborane to yield trialkylcarbinols ($R_3B \longrightarrow R_3COH$) has been studied by Hillman,[1] and particularly by Brown and his colleagues[2,3] who have vividly summarized the unique potentialities of these reactions involving three migrations from boron to carbon.

However, fairly drastic conditions are required, and very recently the Purdue School has shown that the potassium triethylcarboxide-induced reaction of tri-n-butylborane with chlorodifluoromethane followed by oxidation gives a high yield of tri-n-butylmethanol.[4] Chloroform was also used to give a lower but very acceptable yield. Sodium cyanide as one carbon source and trialkylcyanoborates as intermediates have also been shown to give high yields of ketones and carbinols[5,6] (Scheme 2).

Scheme 2

The reaction can be controlled at different stages to give aldehyde, ketone, primary or secondary alcohols[3,6] (Scheme 3).
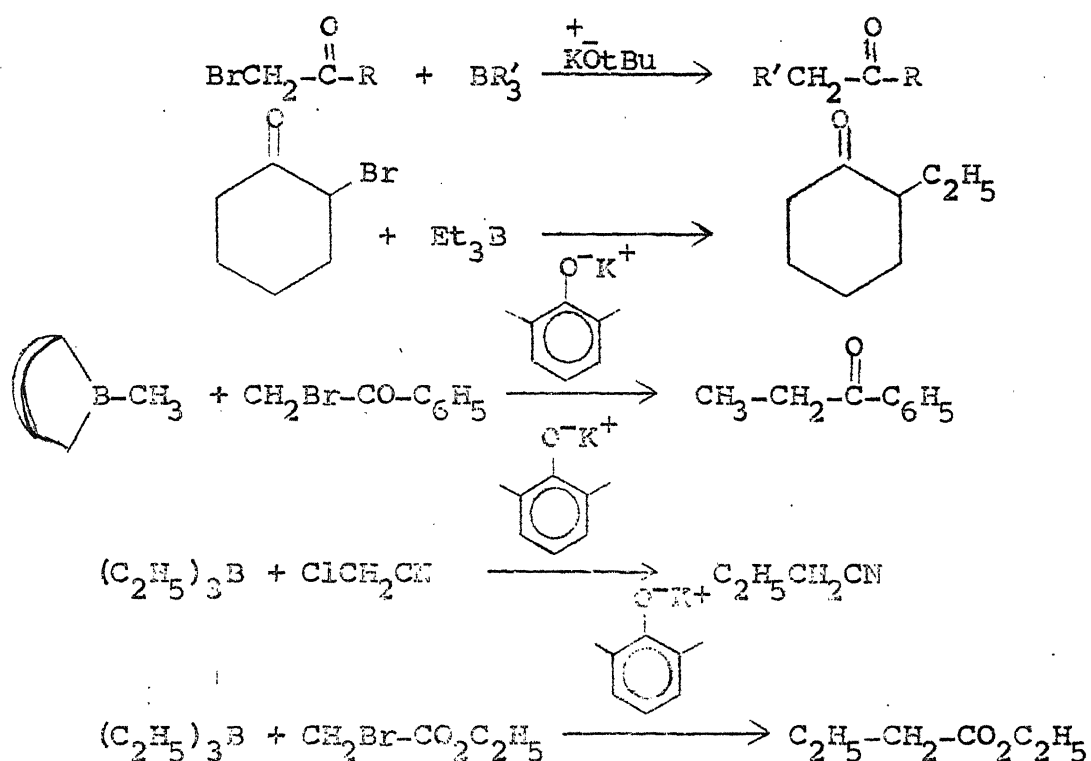
Scheme 3
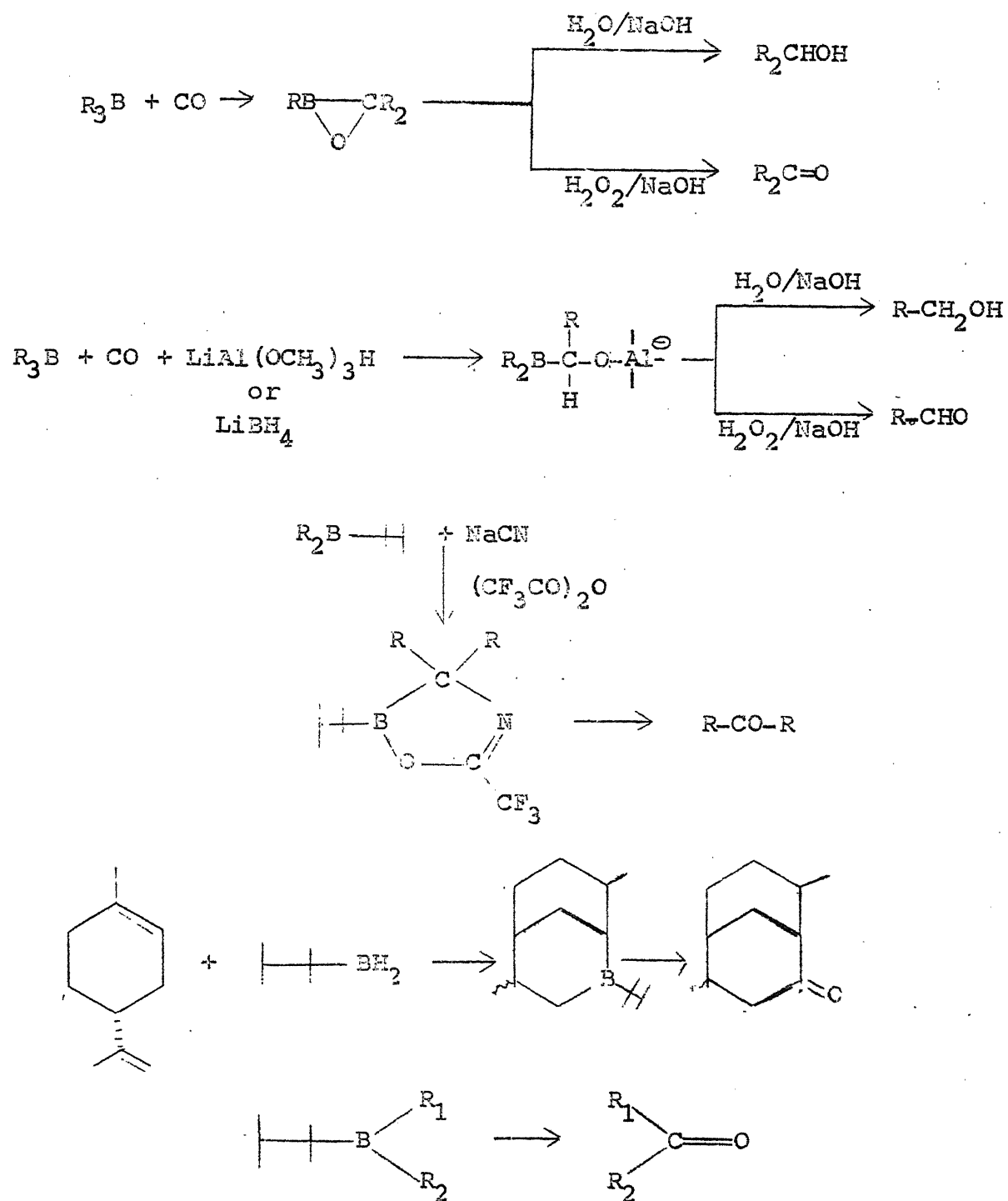
Thus, the reaction of organoboranes with carbon monoxide in the presence of lithium trialkylaluminium hydride provides a convenient method for a one-carbon homologation.[3] Similarly, two-carbon homologation has been achieved by the reaction of organoboranes with ethyl bromoacetate under the influence of a base,[7-10] with ethyl diazoacetate[11,12] or with other acetic acid derivatives, ketones and aldehydes (Scheme 4).
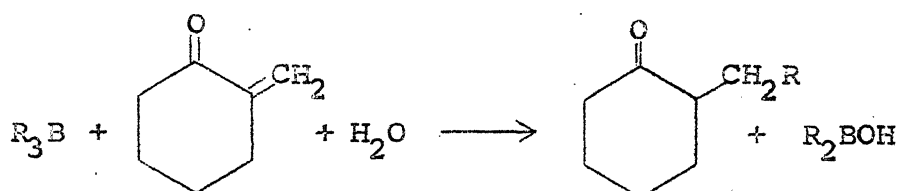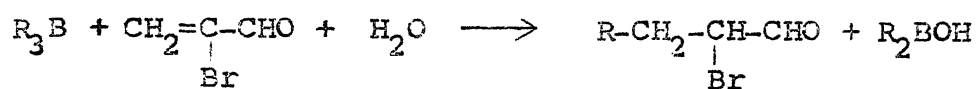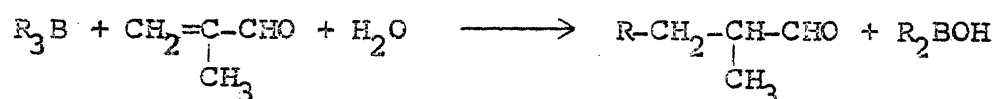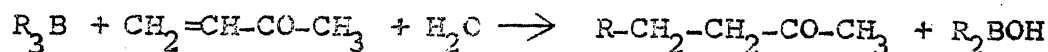
<u>Scheme 4</u>

$$BrCH_2-\overset{\overset{\text{O}}{\|}}{C}-R \ + \ BR_3' \ \xrightarrow{\overset{+}{K}\overset{-}{O}tBu} \ R'CH_2-\overset{\overset{\text{O}}{\|}}{C}-R$$

$$B-CH_3 \ + \ CH_2Br-CO-C_6H_5 \ \xrightarrow{O^-K^+} \ CH_3-CH_2-\overset{\overset{\text{O}}{\|}}{C}-C_6H_5$$

$$(C_2H_5)_3B \ + \ ClCH_2CN \ \xrightarrow{O^-K^+} \ C_2H_5CH_2CN$$

$$(C_2H_5)_3B \ + \ CH_2Br-CO_2C_2H_5 \ \longrightarrow \ C_2H_5-CH_2-CO_2C_2H_5$$

The reaction of organoboranes with acrolein and α-bromo-acrolein provides a simple 3-carbon homologation.[13-16] Infact, a wide variety of substituted aldehydes and ketones are conveniently synthesized by the reaction of organoboranes with

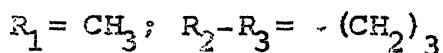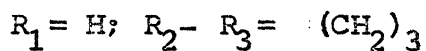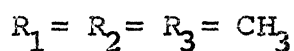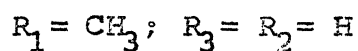α, β -unsaturated ketones and aldehydes (Scheme 5).

Scheme 5

$$R_3B + CH_2=CH-CO-CH_3 + H_2O \longrightarrow R-CH_2-CH_2-CO-CH_3 + R_2BOH$$

$$R_3B + CH_2=CH-CHO + H_2O \longrightarrow R-CH_2-CH_2-CHO + R_2BOH$$

$$R_3B + CH_2=\underset{\underset{CH_3}{|}}{C}-CHO + H_2O \longrightarrow R-CH_2-\underset{\underset{CH_3}{|}}{CH}-CHO + R_2BOH$$

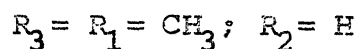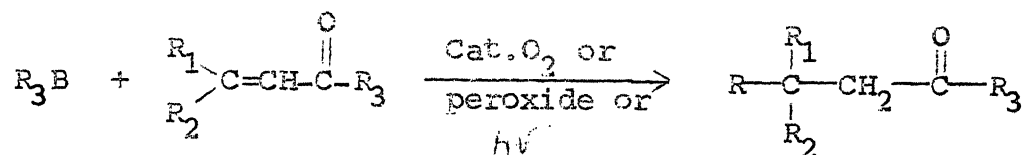$$R_3B + CH_2=\underset{\underset{Br}{|}}{C}-CHO + H_2O \longrightarrow R-CH_2-\underset{\underset{Br}{|}}{CH}-CHO + R_2BOH$$

The presence of 5 mol % of galvinoxyl was shown to inhibit completely the otherwise fast reactions of organoboranes with acrolein and related α, β -unsaturated ketones.[17] Consequently the involvement of a free-radical chain mechanism was proposed for the facile 1,4-addition reactions. The α, β -unsaturated ketones with one or more alkyl substituents in the terminal group fail to react with trialkylborane under the usual conditions. However, the addition of trialkylborane to these α, β -unsaturated aldehydes and ketones has readily been achieved by the addition of catalytic quantities of diacyl peroxides,
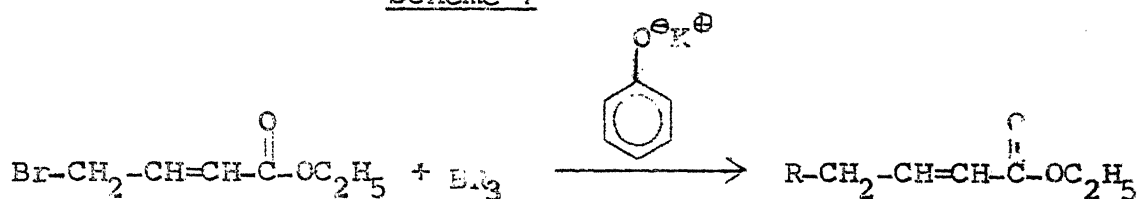
oxygen or by photochemical activation[18,19] (Scheme 6).

Scheme 6

$$R_3B \ + \ \underset{R_2}{\overset{R_1}{>}}C=CH-\overset{\overset{O}{\|}}{C}-R_3 \quad \xrightarrow[h\nu]{Cat.O_2 \ or \ peroxide \ or} \quad R-\underset{\overset{|}{R_2}}{\overset{\overset{R_1}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-R_3$$

$R_3 = R_1 = CH_3; \ R_2 = H$

$R_1 = CH_3; \ R_3 = R_2 = H$

$R_1 = R_2 = R_3 = CH_3$

$R_1 = H; \ R_2 - R_3 = \ (CH_2)_3$

$R_1 = CH_3; \ R_2 - R_3 = \ - (CH_2)_3$

A four-carbon atom homologation has been carried out by the reaction of organoboranes with ethyl 4-bromocrotonate under the influence of 2,6-di-t-butylphenoxide;[20] another example of the versatility of synthetic procedure based on organoborane chemistry (Scheme 7).
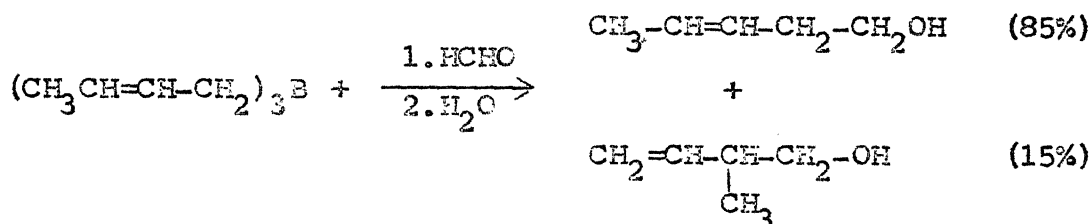
Scheme 7

$$Br-CH_2-CH=CH-\overset{\overset{O}{\|}}{C}-OC_2H_5 \ + \ BR_3 \quad \xrightarrow{\overset{O^{\ominus}K^{\oplus}}{\bigcirc}} \quad R-CH_2-CH=CH-\overset{\overset{O}{\|}}{C}-OC_2H_5$$
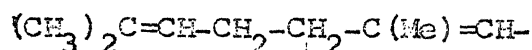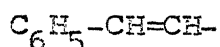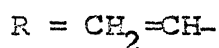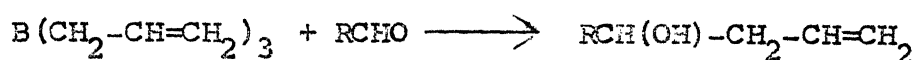
Saturated ketones, aldehydes, alcohols and water are not known to cleave carbon-boron bond of the trialkylboranes.
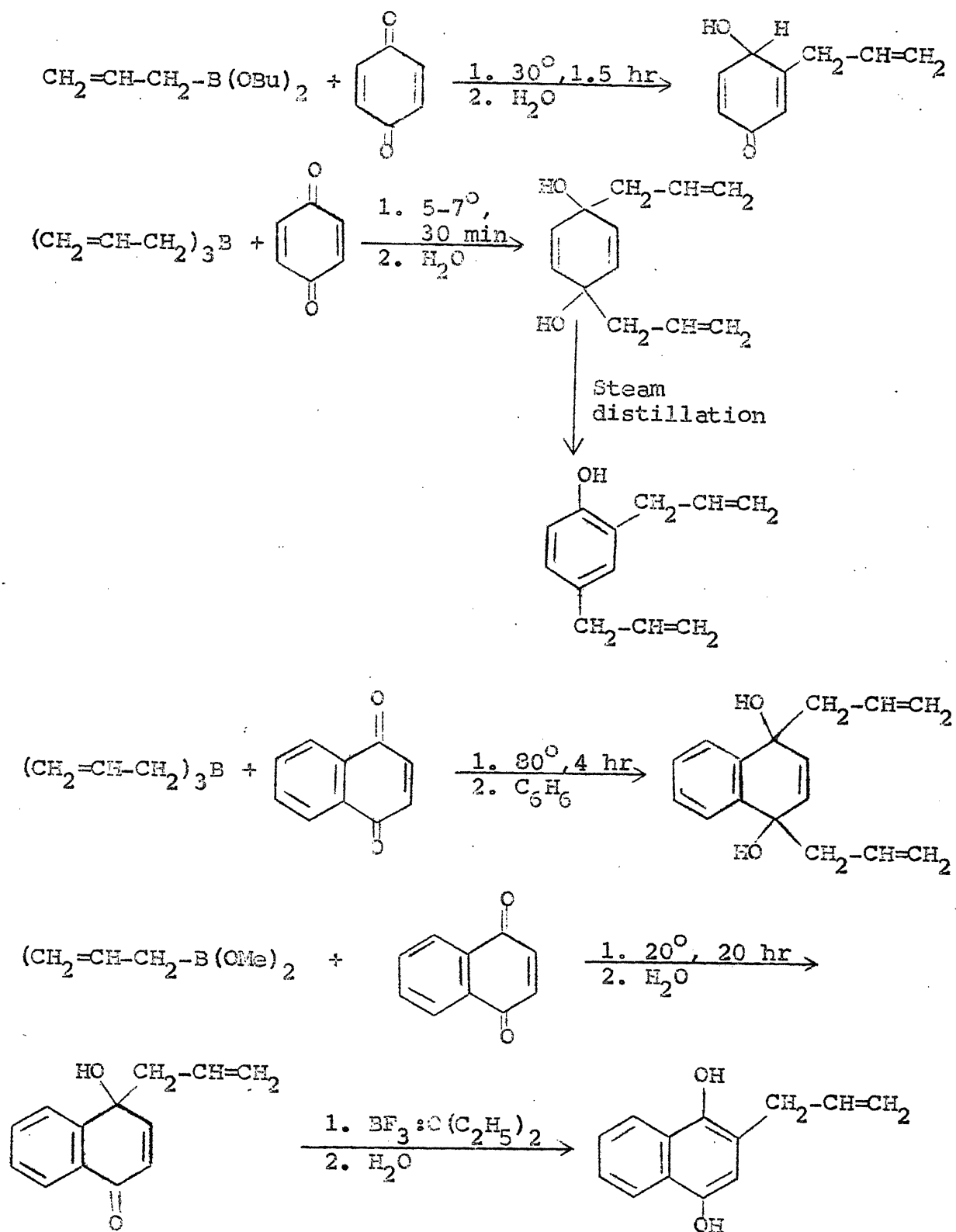
A triallylborane is much more reactive as compared to trialkyl-borane, and a facile reaction is feasible with water,[21] alcohols,[21-22] aldehydes,[21-23] quinones,[24,25] acetylene,[26,27] nitriles,[28] activated olefins[29] and cyclopropenes.[30] An equimolar mixture of triallylborane and α,β-unsaturated aldehydes in ether gives 65-70% of β,γ-unsaturated alcohols.[22] Tricrotylborane in hexane with dry formaldehyde on cooling gave 15% of the product derived from the allylic rearrangement.[21] Hydrolysis of the reaction mixture gave 3-penten-1-ol and 2-methyl-3-buten-1-ol (Scheme 8).

Scheme 8

$$B(CH_2-CH=CH_2)_3 + RCHO \longrightarrow RCH(OH)-CH_2-CH=CH_2$$

$$R = CH_2=CH-$$
$$C_6H_5-CH=CH-$$
$$(CH_3)_2C=CH-CH_2-CH_2-C(Me)=CH-$$

$$(CH_3CH=CH-CH_2)_3B + \xrightarrow[2.H_2O]{1.HCHO}$$

$$CH_3-CH=CH-CH_2-CH_2OH \quad (85\%)$$
$$+$$
$$CH_2=CH-CH-CH_2-OH \quad (15\%)$$
$$\overset{|}{CH_3}$$

A variety of products is derived from the reaction of allyl-boron compound with benzo- and naphthoquinones depending upon the conditions and reactants used[24,25] (Scheme 9).

Scheme 9

$CH_2=CH-CH_2-B(OBu)_2$ + $\xrightarrow[\text{2. } H_2O]{\text{1. } 30^\circ, 1.5 \text{ hr}}$

$(CH_2=CH-CH_2)_3B$ + $\xrightarrow[\text{2. } H_2O]{\substack{\text{1. } 5-7^\circ, \\ 30 \text{ min}}}$

Steam
distillation

$(CH_2=CH-CH_2)_3B$ + $\xrightarrow[\text{2. } C_6H_6]{\text{1. } 80^\circ, 4 \text{ hr}}$

$(CH_2=CH-CH_2-B(OMe)_2$ + $\xrightarrow[\text{2. } H_2O]{\text{1. } 20^\circ, 20 \text{ hr}}$

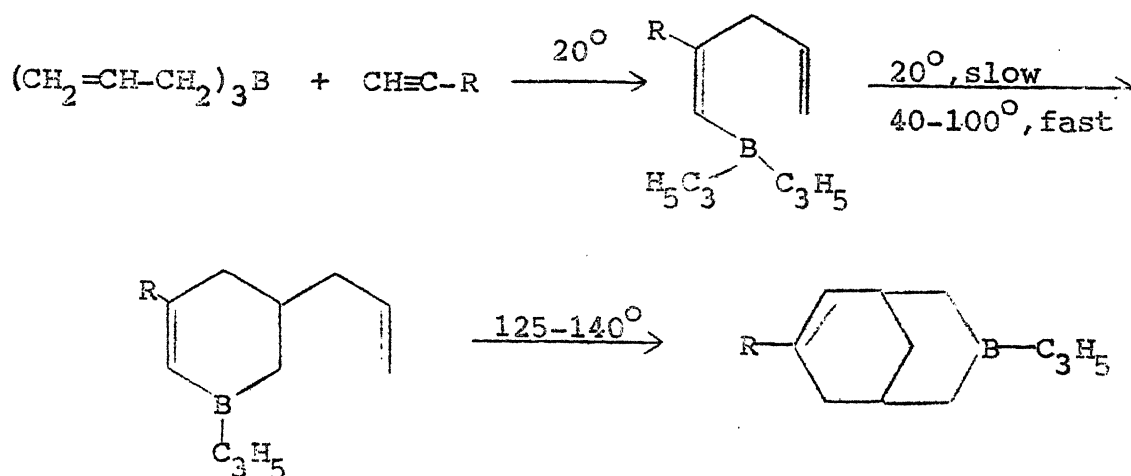 $\xrightarrow[\text{2. } H_2O]{\text{1. } BF_3 \cdot O(C_2H_5)_2}$

The reactions follow a path which involves the initial attack of the allyl moiety at the carbon of carbonyl followed by rearrangement.
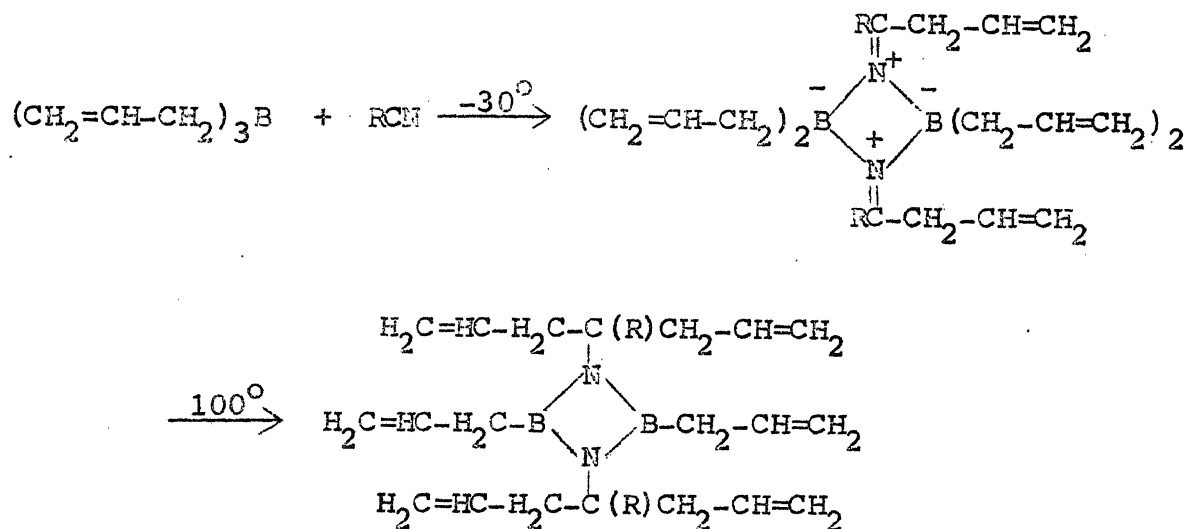
The reaction with acetylene proceeds in three stages[26,27] The first stage is the allylboration of the triple bond of acetylenic compound (R-C≡CH) which results in diallyl(2-$\underline{n}$-butyl-1,4-pentadienyl)borane. This undergoes gradual cyclization $\underline{via}$ allyl rearrangement to give 3-alkyl-1,5-diallyl-1-bora-2-cyclo-hexene. The final stage is the thermal isomerization of 3-alkyl-1,5-diallyl-1-bora-2-cyclohexene to 7-alkyl-3-allyl-3-borabicyclo (3.3.1)non-6-ene (Scheme 10).

Scheme 10

$$(CH_2=CH-CH_2)_3B + CH\equiv C-R \xrightarrow{20^O} \qquad \xrightarrow[40-100^O, fast]{20^O, slow}$$


$$\xrightarrow{125-140^O}$$

Reaction of allyl nitriles[28] with triallylborane at -30° gave an air stable derivative of 2,2,4,4-tetraallylcyclodibora-zane, which when heated to 100° was converted completely into 1,3-bis(diallylmethyl-2,4-diallyl-1,3,2,4-diazadiboratidines (Scheme 11).

Scheme 11

$$(CH_2=CH-CH_2)_3B \quad + \quad RCN \xrightarrow{-30^{\circ}} (CH_2=CH-CH_2)_2B \overset{\overset{\displaystyle RC-CH_2-CH=CH_2}{\underset{+}{\overset{\parallel}{N}}}}{\underset{\underset{RC-CH_2-CH=CH_2}{\overset{\parallel}{N}}}{\square}} B(CH_2-CH=CH_2)_2$$

$$\xrightarrow{100^{\circ}} \quad H_2C=HC-H_2C-B \overset{\overset{\displaystyle H_2C=HC-H_2C-C(R)CH_2-CH=CH_2}{\underset{N}{\overset{\parallel}{N}}}}{\underset{\underset{H_2C=HC-H_2C-C(R)CH_2-CH=CH_2}{N}}{\square}} B-CH_2-CH=CH_2$$

Allylboration of activated olefins such as vinyl ethers and methylcyclopropene[30] leads to the formation of 1,4- and 1,5-dienes (Scheme 12).

Scheme 12
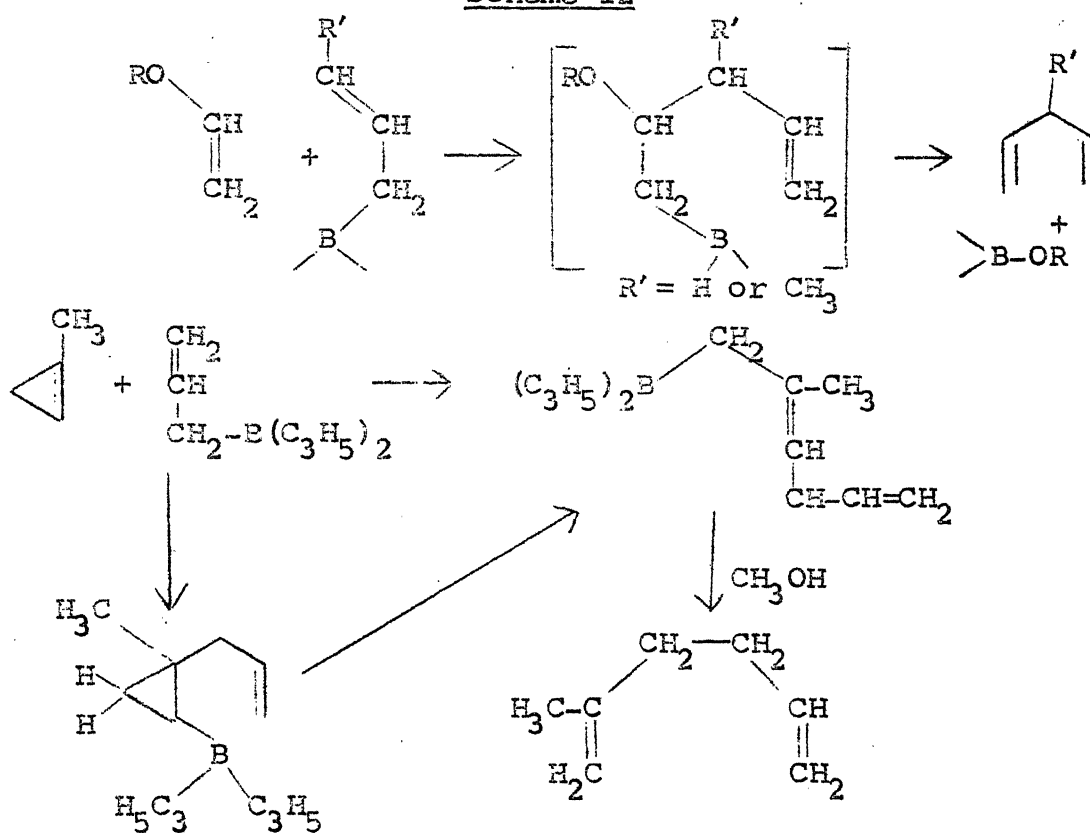
From the studies on the reactions of triallylborane, it
is very difficult to examine the extent of allylic rearrangement
by simple means. It therefore appeared of interest to synthe-
size and study some of the reactions of a substituted allyl-
borane. We wanted to examine the possibilities of the mechanism
as well as the synthetic utility of these reactions. The present
work deals with the synthesis and reactions of disiamyl(3-phenyl-
2-butenyl)borane (DSPBB) with aliphatic aldehyde (butyraldehyde),
aromatic aldehyde (benzaldehyde), α,β-unsaturated aldehyde
(acrolein) and aliphatic ketone (acetone). We thought that the
examination of the reactions of DSPBB with α,β-unsaturated
aldehyde would reveal the difference in reactivity between
alkyl and alkenyl groups and also the type of addition react-

## V.3 RESULTS AND DISCUSSION

The allene, 3-phenyl-1,2-butadiene was synthesized in
the conventional manner starting from α-methyl styrene
(Scheme 13). α-Methyl styrene (1) was converted into 1,1-dibromo-
2-phenyl-2-methylcyclopropane (2) by the reaction with bromoform
and potassium-t-butoxide. The resulting 1,1-dibromocyclopropane
derivative (2) was treated with methyllithium in ether at-40 to
-50° to give 3-phenyl-1,2-butadiene (3) in good yield. The
properties of the compound corresponded well with those reported
in the literature.[31]

Disiamylborane (4) was prepared by the hydroboration
of 2-methyl-2-butene (5) with borane solution in tetrahydrofuran

Scheme 13
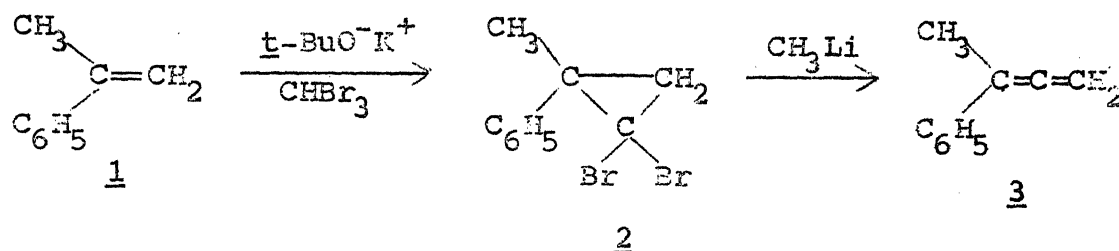
under a static pressure of nitrogen[32] (Scheme 14). A solution of
3-phenyl-1,2-butadiene (3) in dry tetrahydrofuran was added to
the above solution within 5 min and was allowed to attain room
temperature to give disiamyl(3-phenyl-2-butenyl)borane (DSPBB)
(6) as a major product along with small amount of vinyl organo-
borane (7). The resulting mixture (6 and 7) was treated with
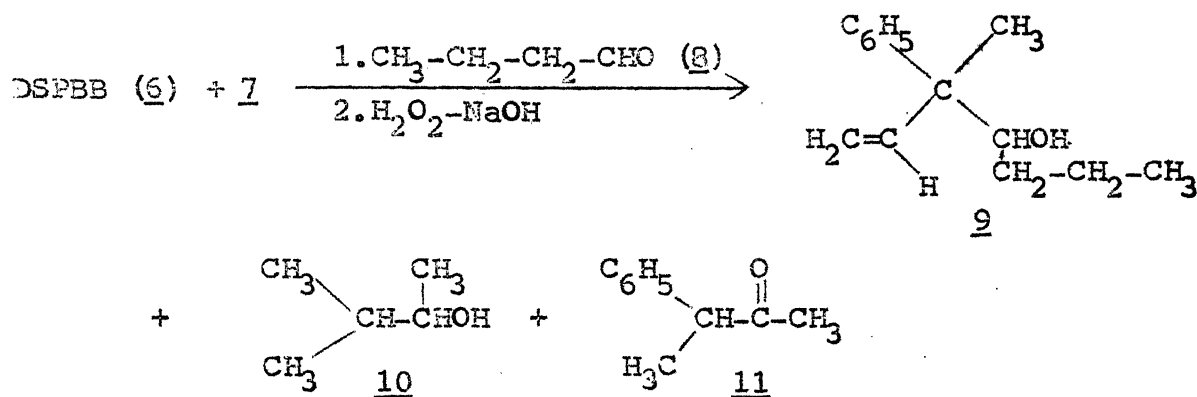
Scheme 14
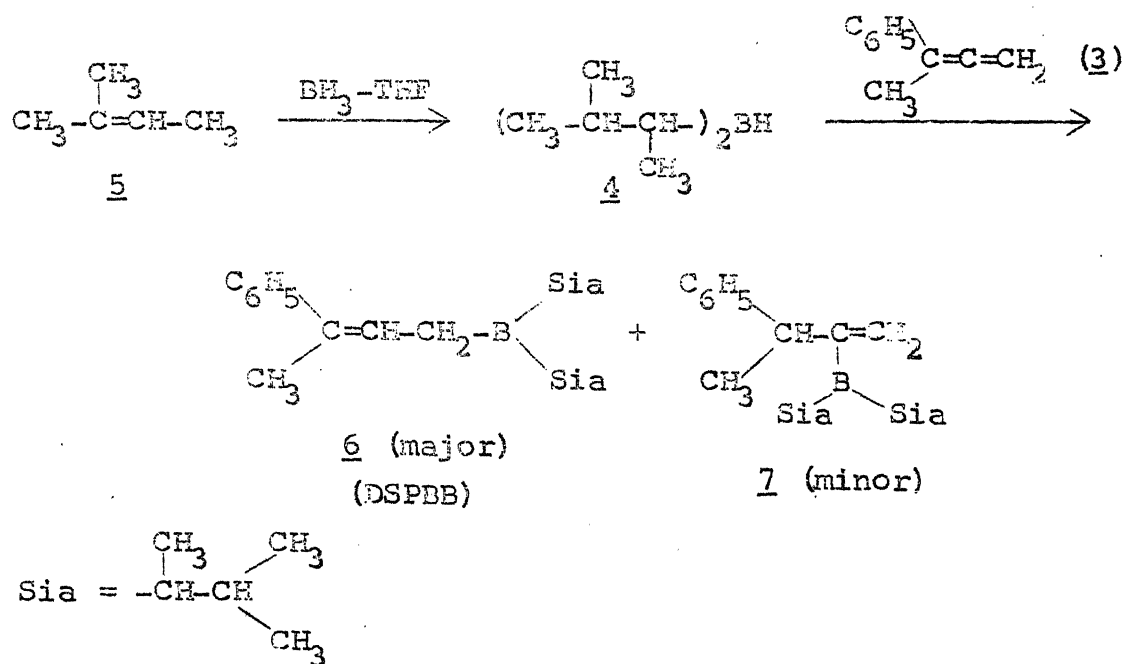
appropriate aldehyde or ketone, allowed to stir for the required time, and oxidized with alkaline hydrogen peroxide. The products were analyzed by GLC or TLC and pure compounds were obtained by preparative GLC using a silicone rubber column or by column chromatography on basic alumina and identified by elemental analysis, IR and NMR.

V.3.1   Reaction of DSPBB (6) with Butyraldehyde (8)

The reaction of DSPBB (6) with butyraldehyde (8) followed by hydrolysis and oxidation provided 3-methyl-3-phenylhept-1-en—4-ol (9) in addition to the expected siamyl alcohol (10) and a small amount of 3-phenyl-2-butanone (11) (Scheme 15). The formation of 10 suggests that it is arising from the oxidation of the siamyl groups of 6 and 7. The presence of small amount of 11 reveals that it is formed from the oxidation of vinyl-borane 7, obtained by the central attack of boron on the allenic linkage[33] in 3. The yield of 9 based on column chromatography separation was 60%. The structure was assigned on the basis of correct elemental analysis IR and NMR.

Scheme 15

$$DSPBB \ (\underline{6}) + \underline{7} \quad \xrightarrow[\text{2.H}_2\text{O}_2\text{-NaOH}]{\text{1.CH}_3\text{-CH}_2\text{-CH}_2\text{-CHO} \ (\underline{8})}$$

IR spectrum showed characteristic bands at 3500, 1040 due to alcoholic group; 989, 920 cm^{-1} assigned to terminal double bond and 1600 cm^{-1} due to aromatic ring. NMR spectrum had signals at δ 7.4 (m, 5H) aromatic protons, 6.25 (dd, J_c = 8.0 Hz and J_t = 11.0 Hz, 1H) olefinic methine proton, 5-5.4 (m, 2H) terminal methylene protons, 3.9 (m, 1H) methine proton and 10-10.4 (m, 11H) methyl, methylene and hydroxyl protons.

V.3.2 Reaction of DSPBB (6) with Benzaldehyde (12)

The hydroborated mixture (6 and 7) on treatment with benzaldehyde (12) followed by hydrogen peroxide oxidation afforded 1,2-diphenyl-2-methylbut-3-en—1-ol (13) in 65% yield along with 10 and 11 (Scheme 16). The structure of 13 was confirmed by elemental analysis, IR and NMR.

Scheme 16

DSPBB (6) + 7 $\xrightarrow[\text{2. } H_2O_2\text{-NaOH}]{\text{1. } C_6H_5CHO \ (12)}$

+ 10 + 11

13
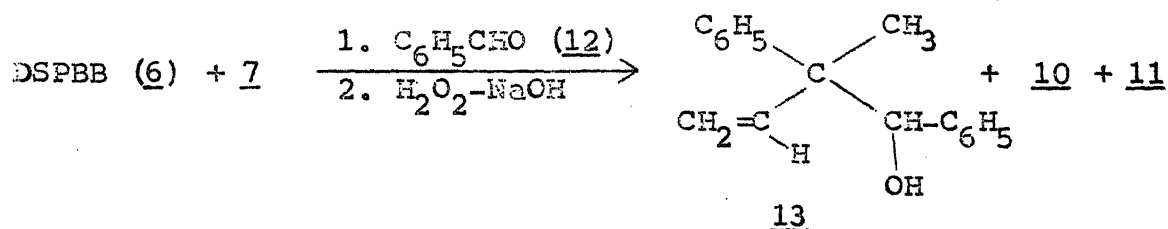
IR spectrum had bands at 3500, 1030 (alcoholic group), 3030, 1600, 720 (aromatic ring); 915 and 1000 cm^{-1} (terminal olefin). NMR spectrum showed signals at δ 7.3-7.5 (m,10H) aromatic protons, 6.46 (dd, J = 8.0 Hz, J = 11.0 Hz, 1H) olefinic methine proton, 5.2 (m,3H), terminal methylene and benzylic protons,

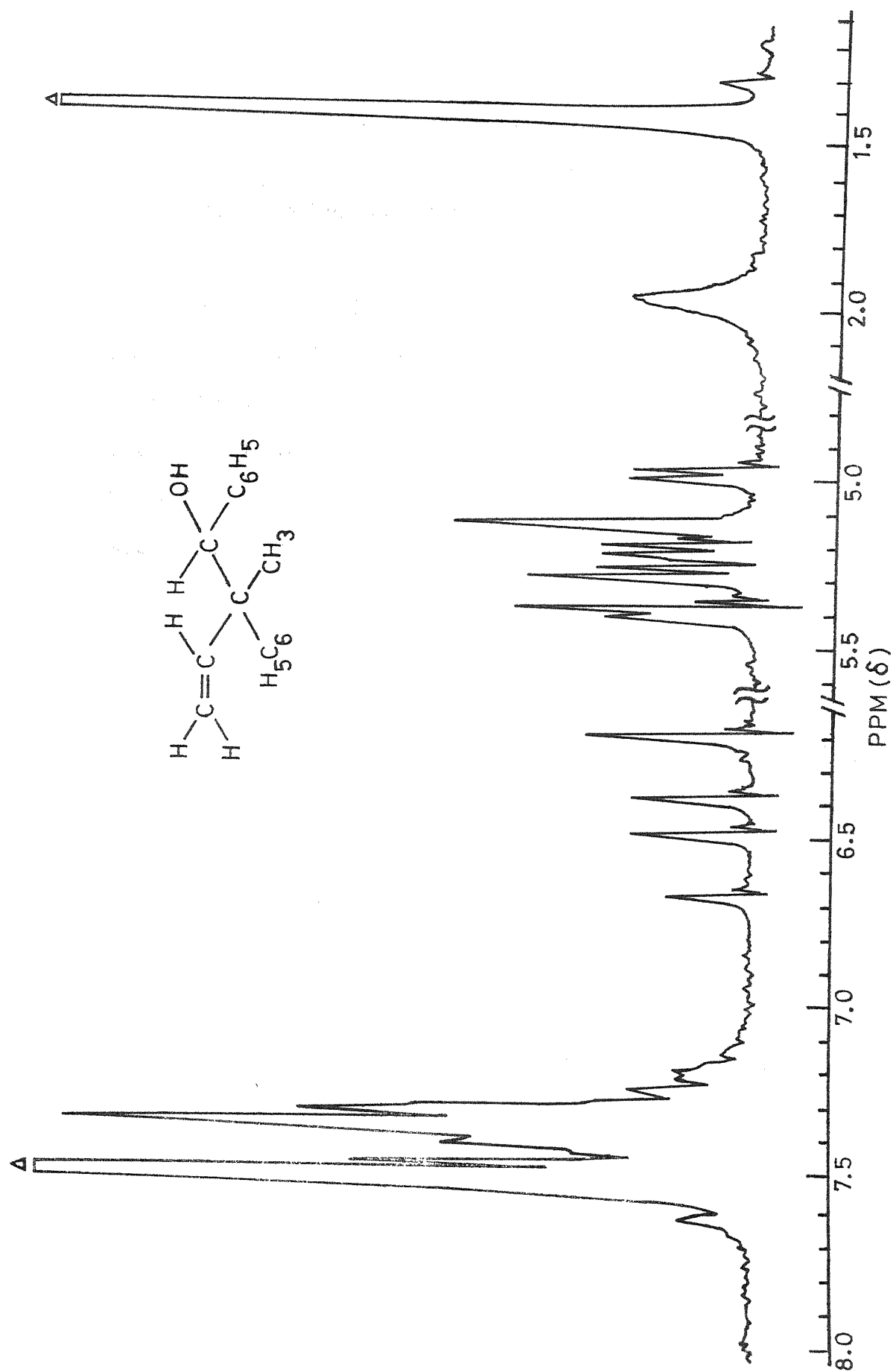Figure V.2: NMR Spectrum of 1,2-diphenyl-2-methylbut-3-en-1-ol (13)

1.96 (s, 1H) hydroxyl proton and 1.4 (s, 3H) methyl protons.

V.3.3 Reaction of DSPBB (6) with Acrolein (14)

Acrolein (14) with DSPBB (6) leads to the formation of 4-phenyl-4-methyl-1,5-hexadien-3-ol (15) in 60% yield (Scheme 17). IR spectrum showed absorptions at 3500, 1040 (alcohol), 3050, 1600, 700 (aromatic), 990 and 920 cm^{-1} (terminal double bond). NMR spectrum had bands at δ 7.3 (m, 6H) aromatic plus hydroxyl protons, 6.2 (dd, $J_t = 11.0$ Hz, $J_c = 8.0$ Hz, 1H) methine olefinic proton attached to benzylic carbon, 5.70 (dd, $J_c = 5.0$ Hz, $J_t = 10.0$ Hz, 1H), 5.25 (cm, 4H) terminal methylene protons, 4.4 (bd, 1H) allylic methine proton, and 1.4 (s, 3H) methyl protons.

Scheme 17
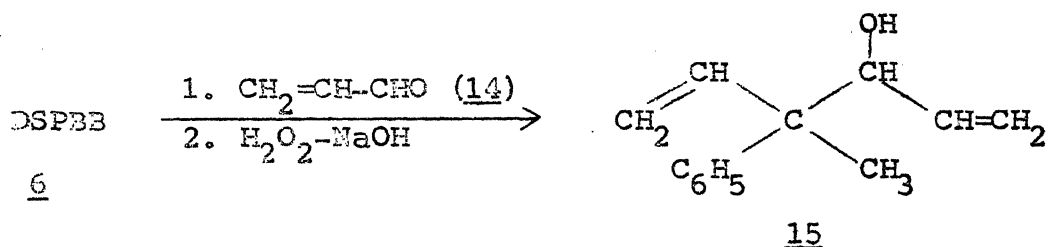
V.3.4 Reaction of DSPBB (6) with Acetone (16)

The reaction of acetone (16) with 6 leads to the formation of a tertiary alcohol, 2,3-dimethyl-3-phenylpent-4-en-2-ol (17) in 60% (Scheme 18). The structure of 17 was assigned based on elemental analysis, IR and NMR. IR spectrum of 17 had usual bands for alcoholic, aromatic and terminal olefinic groups. NMR showed signals at δ 7.3 (s, 5H) aromatic protons,
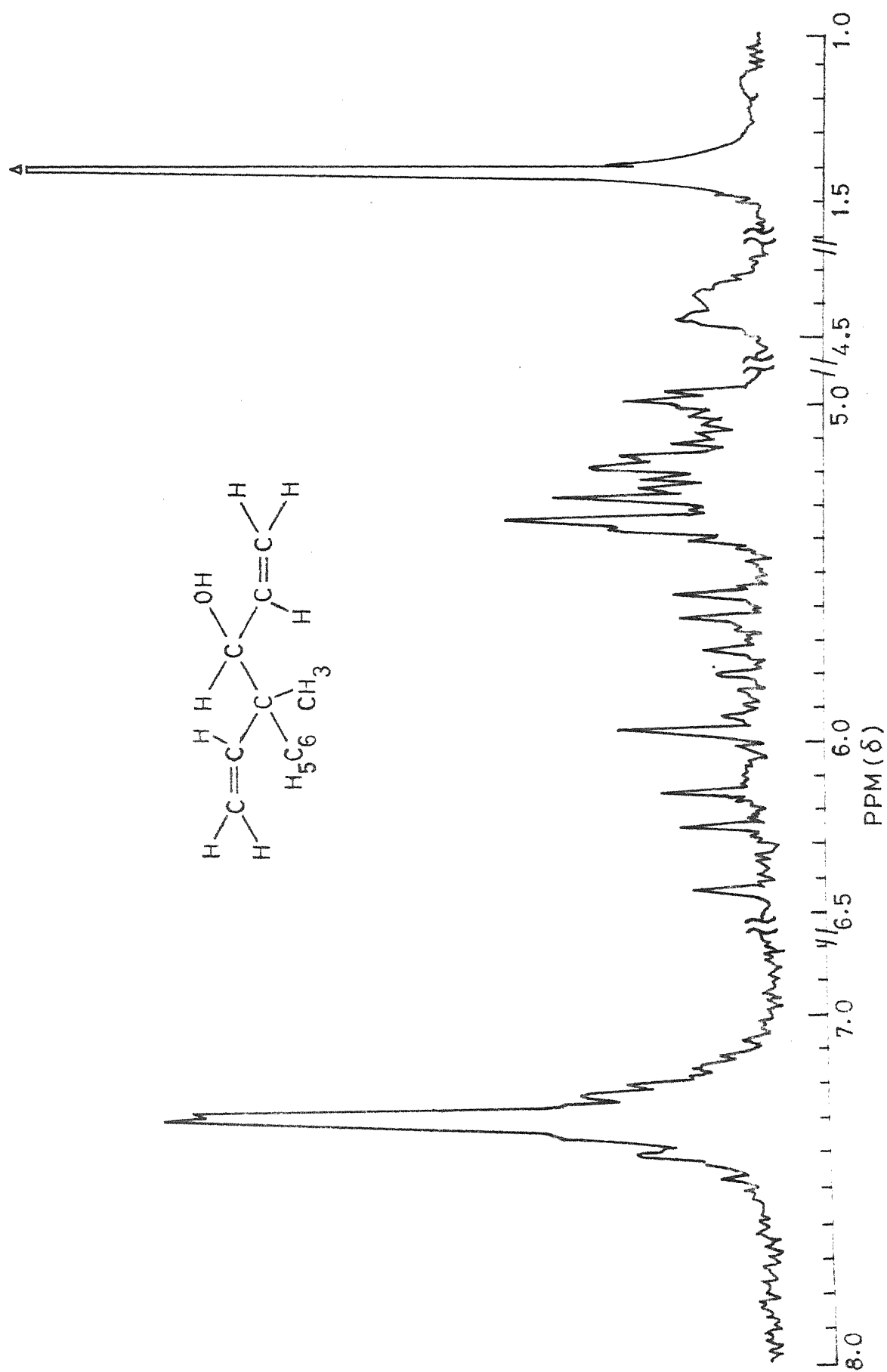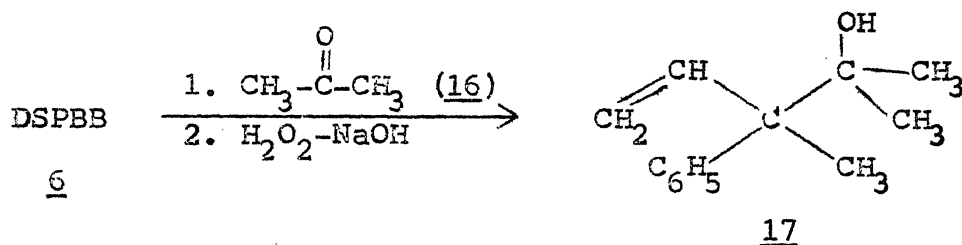
Figure V. 3: NMR spectrum of 4-phenyl-4-methyl-1,5-hexadien-3-ol (15)

Scheme 13

DSPBB $\xrightarrow[\text{2. } H_2O_2\text{-NaOH}]{\text{1. } CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 \quad (\underline{16})}$

$\underline{6}$

17

6.55 (dd, J_c = 8.0 Hz, J_t = 11.0 Hz, 1H) olefinic methine proton, 5.35–4.9 (m, 2H) terminal methylene protons, 1.6 (s, 4H), methyl and hydroxyl protons, 1.18 (s, 3H) methyl protons and 1.10 (s, 3H) methyl protons.

The DSPBB (6) underwent a remarkably ready reaction with butyraldehyde (8), benzaldehyde (12) and acrolein (14). However, the reaction with acetone (16) was found to be slow. With aldehydes the reaction was complete within one hour whereas acetone took about 12 hr at 60° for completion of the reaction. This indicates that aldehydes are more reactive than ketones towards 6. There is a marked difference between the reaction of acrolein with trialkylborane and DSPBB. In the case of DSPBB (6) no product was obtained corresponding to the attack of siamyl group or allyl group at the β-position of acrolein. However, trialkylboranes react with acrolein to give a product resulting from 1,4-addition.[17] A cyclic transition was assumed for such a reaction by Brown and coworkers,[16] consistent with the 1,4-addition mechanism of the Grignard reagent to
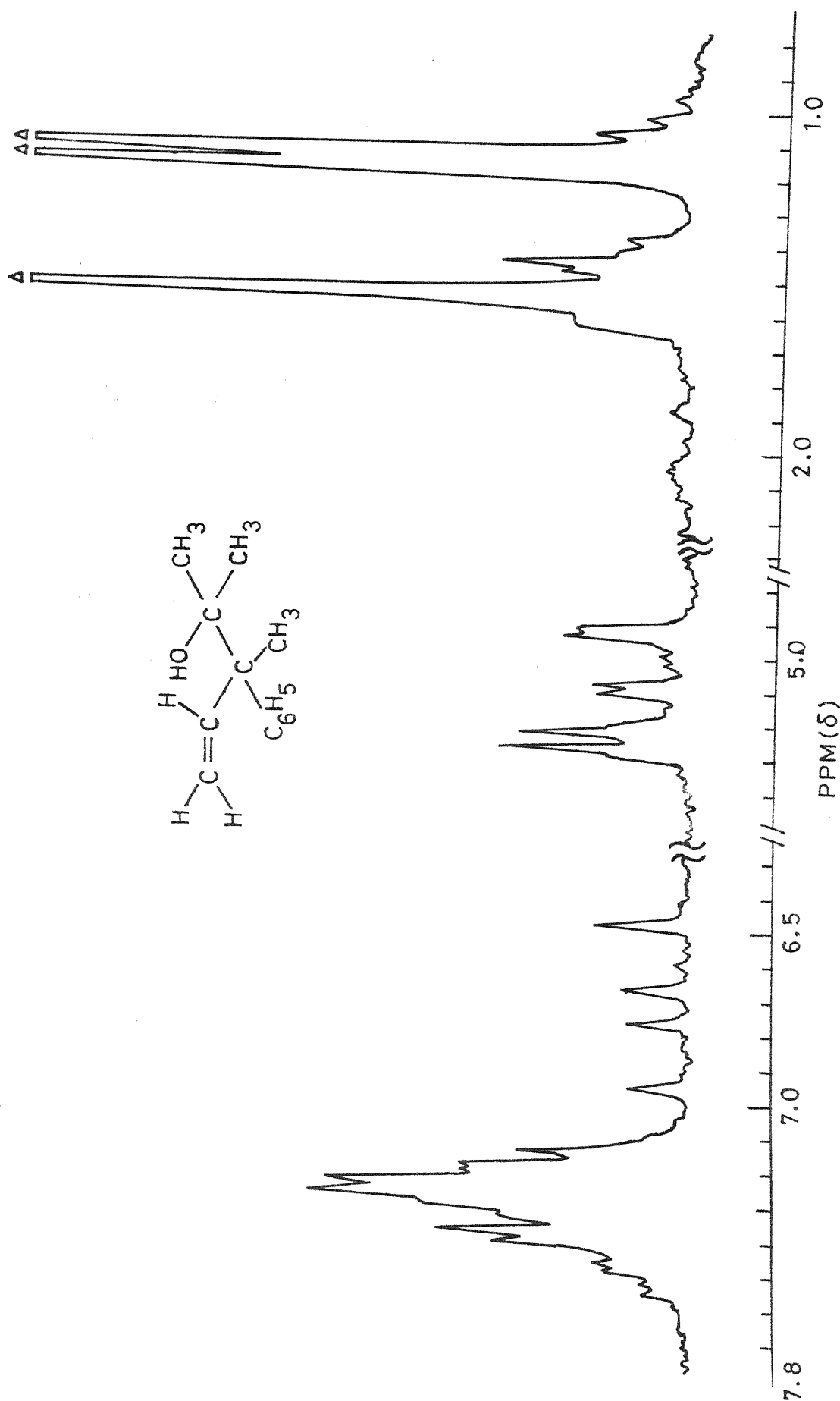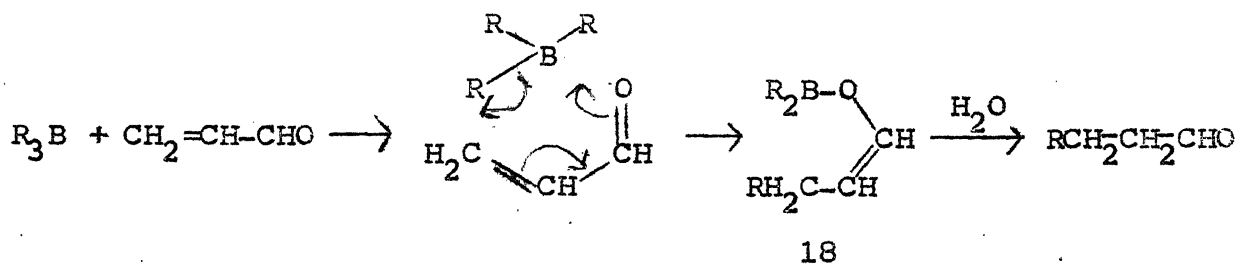
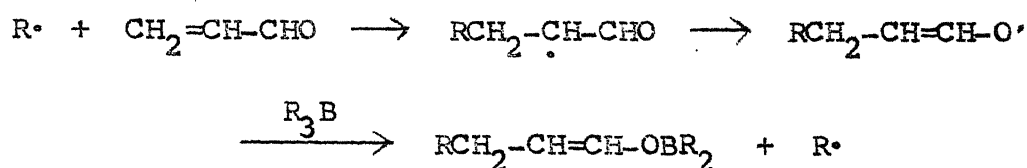Figure V.4: NMR Spectrum of 2,3-dimethyl-3-phenylpent-4-en-2-ol (17)

α,β-unsaturated ketones.[34,35] The reaction of trialkylborane with acrolein in absence of water or other protonolyzing species, leads to the formation of an enol borinate (18), which is rapidly hydrolyzed to the corresponding aldehyde[13,14] (Scheme 19).

Scheme 19

$$R_3B + CH_2{=}CH{-}CHO \longrightarrow \quad\quad \longrightarrow \quad\quad \xrightarrow{H_2O} RCH_2CH_2CHO$$

18

The formation of 18 is quite consistent with the proposed cyclic mechanism. However, the non-reactivity of β-alkyl substituted γ,β-unsaturated aldehydes is not explicable through such a cyclic mechanism. Alternatively, a free radical chain mechanism similar to the copper catalyzed 1,4-addition of Grignard reagent to α,β-unsaturated aldehyde[36-40] was speculated in accordance with the experimental results[18,19] (Scheme 20).

Scheme 20

$$R{\cdot} + CH_2{=}CH{-}CHO \longrightarrow RCH_2{-}\underset{\bullet}{CH}{-}CHO \longrightarrow RCH_2{-}CH{=}CH{-}O{\cdot}$$
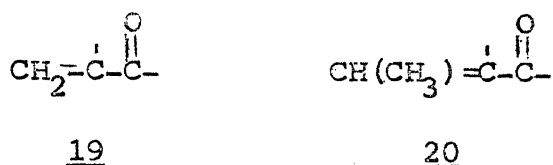
$$\xrightarrow{R_3B} RCH_2{-}CH{=}CH{-}OBR_2 + R{\cdot}$$

Evidently, the kinetic chain length for the addition of a free-

radical[17] to a terminal unsubstituted grouping (19) is much
more longer than for the corresponding addition to the substi-
tuted grouping (20) (Scheme 21).

Scheme 21

$$CH_2=\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{}}}{\underset{}{C}-C-}$$ $$CH(CH_3)=\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{}}}{\underset{}{C}-C-}$$

19   20

Our results on the reaction of DSPBB with aldehydes and
ketones clearly indicate that the reaction involves the migration
of 3-phenyl-2-butenyl with rearrangement in preference to the
siamyl group. Based on these observations, the formation of
the olefinic alcohols can best be visualized through a six-
membered cyclic transition state (21) rather than a non-cyclic
S_E2' process[41] (22) or a radical addition mechanism (Scheme 22).

Scheme 22

21   22
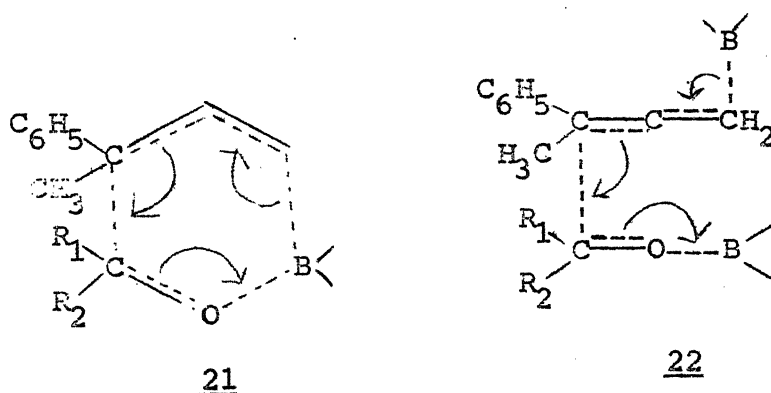
This proposal is further substantiated by the following facts:

(i) No 1,4-addition product is formed with acrolein. (ii) No reaction takes place with ethyl acetate or ethyl acrylate even in the presence of the added nucleophile like sodium acetate. (iii) Formation of only rearrangement product in every case. (iv) The reactivity difference between aldehydes and ketones.

Finally, from the point of organic synthesis, the reactions with aldehydes and ketones provide a convenient method to synthesize β , γ -unsaturated alcohols. Our preliminary dehydration experiments with β , γ -unsaturated alcohols suggest that it is possible to use these unsaturated alcohols in the synthesis of sustituted 1,4-dienes. The reactions of DSPBB (6) with α , β -unsaturated aldehydes give hydroxy group substituted 1,5-dienes which could serve as substrate for Cope's rearrangement. Thus, the reactions of DSPBB (6) with variety of aldehydes, ketones, α , β -unsaturated aldehydes and ketones might provide a good way to synthesize substituted 1,4- and 1,5-dienes.

V.4 EXPERIMENTAL

Boiling points are uncorrected. All infrared (IR) spectra were recorded on a Perkin-Elmer Model 700 spectrophotometer as thin films between sodium chloride plates. Nuclear magnetic resonance (NMR) spectra were taken on a Varian A-60 spectrometer in deuterated chloroform with TMS as the internal standard. Gas liquid chromatographic analyses were done with

Aerograph Model 90-P instrument using 3 ft by 1/4 inch silicone rubber column. Column chromatography was done using basic alumina (E. Merck). Microanalyses were carried out by Mr. A. H. Siddiqui, Microanalyst, Department of Chemistry, Indian Institute of Technology, Kanpur-16, India.

Starting Materials

Butyraldehyde (BDH), benzaldehyde (BDH), acrolein (Fluka-AG) and acetone (BDH) were distilled before use. Other materials were used as described in the experimental part of Chapter III.4.

Preparation of 3-Phenyl-1,2-butadiene

3-Phenyl-1,2-butadiene was prepared by utilizing the same procedure as described earlier in Chapter III.4.

Preparation of Disiamyl(3-phenyl-2-butenyl)borane in Situ

2-Methyl-2-butene (1.4 g, 0.02 mol) in 15 ml dry tetrahydrofuran was placed in a 100 ml three-necked flask fitted with a condenser, an equilibrating dropping funnel, a thermometer and an inlet and an outlet for nitrogen. The flask was immersed in ice bath. To this, 7 ml of 1.6M solution of borane (0.01 mol) in tetrahydrofuran was added maintaining the temperature 0-5°.[32] After allowing the reaction mixture to stand at 0° for 1 hr, 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol) was added within 5 min. The mixture was left for 3 hr to attain room temperature and then stirred for 1 more hr at room temperature to afford mainly disiamyl(3-phenyl-2-butenyl)borane (DSPBB) in tetrahydrofuran.[33]

Reaction of DSPBB with Butyraldehyde

The organoboranes obtained from 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol), 2-methyl-2-butene (1.4 g, 0.02 mol) and 7 ml of 1.6M borane solution in tetrahydrofuran were treated with butyraldehyde (0.72 g, 0.01 mol). The reaction mixture was allowed to stir for 1 hr, hydrolyzed with water and oxidized with alkaline hydrogen peroxide. The usual work-up of the reaction provided 3.0 g of a liquid product. GLC analysis of the liquid product on a 3 ft silicone rubber column showed three components. Two of the three components were identified as 3-phenyl-2-butanone and 3-methyl-2-butanol by comparison of GLC retention times and IR spectra using authentic samples. The third component and 3-phenyl-2-butanone were separated from the mixture by column chromatography on basic alumina. Elution of the column with petroleum ether (60-80°) afforded 0.12 g (8%) of 3-phenyl-2-butanone. The semicarbazone derivative of 3-phenyl-2-butanone had mp and mixture mp, 169-170° (lit[42] mp 173°). Further elution of the column with benzene gave 1.2 g (60%) of a liquid, bp 100-110° (bath temperature) at 1 mm.

IR spectrum showed characteristic bands at 3500, 1040 due to alcoholic group; 989, 920 due to terminal double bond and 1600 cm^{-1} due to aromatic ring. NMR spectrum had signals at δ 7.4 (m, 5H) aromatic protons, 6.25 (dd, J_c= 8.0 Hz and J_t= 11.0 Hz, 1H) olefinic methine proton, 5-5.4 (m, 2H) terminal methylene protons, 3.9 (m, 1H) methine proton, and 10-10.4

(m, 11H) methyl, methylene and hydroxy protons. Thus the compound was identified as 3-methyl-3-phenylhept-1-en—4-ol.

Anal. for $C_{14}H_{20}O$: Calcd: C, 84.35; H, 9.80.

Found: C, 84.20; H, 9.50.

Reaction of DSPBB with Benzaldehyde

Benzaldehyde (1.06 g, 0.01 mol) was added to organoboranes obtained from 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol), 2-methyl-2-butene (1.4 g, 0.02 mol) and 7 ml of 1.6M borane solution in dry tetrahydrofuran. The mixture was stirred for 1 hr and oxidized with alkaline hydrogen peroxide. The usual work-up procedure afforded 3.7 g of viscous oil which gave 0.14 g (10%) of 3-phenyl-2-butanone, and 1.5 g (65%) 1,2-diphenyl-2-methylbut-3-en—1-ol, bp 100° at 0.01 mm.

IR spectrum showed absorptions at 3500, 1030 (alcoholic group); 3030, 1600, 720 (aromatic ring); 915 and 1000 cm^{-1} (terminal olefin). NMR spectrum showed signals at δ 7.3-7.5 (m, 10H) aromatic protons, 6.46 (dd, J_c = 8.0 Hz, J_t = 11.0 Hz, 1H) olefinic methine proton, 5.2 (m, 3H) terminal methylene plus benzylic protons, 1.96 (s, 1H) hydroxyl proton, and 1.4 (s, 3H) methyl protons.

Anal. for $C_{17}H_{18}O$: Calcd: C, 85.71; H, 7.56.

Found: C, 85.40; H, 7.50.

Reaction of DSPBB with Acrolein

To the solution of DSPBB obtained from 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol) was added freshly distilled acrolein

(0.56 g, 0.01 mol) at room temperature. This was allowed to

stir for 1 hr and cooled to $0°$, hydrolyzed and oxidized using

5 ml of 3M sodium hydroxide and 5 ml of 30% w/v hydrogen

peroxide. The usual work-up procedure gave 3.2 g of crude

product. The column chromatographic separation gave 0.14 g

(10%) of 3-phenyl-2-butanone and 1.1 g (60%) of 4-phenyl-4-

methyl-1,5-hexadien-3-ol, bp 90-95° (bath temperature) at 1 mm.

IR spectrum showed bands at 3500, 1040 (hydroxyl); 3050,

1700, 1600 (aromatic ring); 990 and 920 cm^{-1} (terminal olefin).

NMR spectrum had signals at δ 7.3 (m, 6H) aromatic plus hydroxyl

protons, 6.2 (dd, 1H, J_t = 11.0 Hz, J_c = 3.0 Hz) methine olefinic

proton attached to benzylic carbon, 5.70 (dd, 1H, J_t = 10.0 Hz,

J_c = 5.0 Hz), 5.25 (cm, 4H) terminal methylene protons, 4.4 (bd,

1H) allylic methine proton, and 1.4 (s, 3H) methyl protons.

<u>Anal.</u> for $C_{13}H_{16}O$: Calcd: C, 82.97; H, 8.50.

Found: C, 82.96; H, 8.40.

Reaction of DSPBB with Acetone

Acetone (0.58 g, 0.01 mol) was added at room temperature

to the organoboranes obtained from 3-phenyl-1,2-butadiene (1.3 g,

0.01 mol), 2-methyl-2-butene (1.4 g, 0.02 mol) and 7 ml of

1.6M borane solution in dry tetrahydrofuran. The mixture was

refluxed for 12 hr at 70° with stirring and then cooled to 0°.

The usual oxidation and work-up of the reaction products affor-

ded 3 g of a liquid mixture which on column chromatographic

separation gave 0.14 g (10%) of 3-phenyl-2-butanone and 1.0 g

(60%) of 2,3-dimethyl-3-phenylpent-4-en-2-ol, bp 90-95°

(bath temperature) at 1 mm.

IR spectrum showed strong bands at 3500, 1030 (alcoholic group); 3030, 1600, 720 (phenyl ring); 1000 and 915 cm^{-1} (terminal methylene). NMR showed signals at δ 7.3 (s, 5H) aromatic protons, 6.55 (dd, $J_c = 8.0$ Hz and $J_t = 11.0$ Hz, 1H) olefinic methine proton, 5.35-4.9 (m, 2H) terminal methylene protons, 1.6 (s, 4H) methyl and hydroxyl protons, 1.18 (s, 3H) methyl protons and 1.10 (s, 3H) methyl protons.

Anal. for $C_{13}H_{18}O$: Calcd: C, 82.10; H, 9.47.

Found: C, 82.19; H, 9.50.

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VITAE

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